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Modelling the Peeling Behavior of Soft Adhesives

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Abstract

Peel tests were performed on pharmaceutical drug patches which consisted of a polyester backing membrane supporting an acrylic pressure-sensitive adhesive (PSA) (without and with an anti-fungal drug present) adhered to a polyethylene substrate. Interfacial separation of the PSA from the polyethylene substrate was observed in most cases. Finite element (FE) peeling simulations were conducted which characterized the backing-membrane as an elasto-plastic power-law material, the PSA as a viscoelastic material and the interfacial properties with a cohesive zone model (CZM). The mechanical response of the backing membrane and the PSA were measured from tensile experiments while the rate-dependent cohesive zone parameters, i.e. the fracture energy and maximum stress, were measured directly from poke-chip probe tack tests. The numerical results from the CZM/FE simulations and the experimental values of the peel forces as a function of the peel angle, peel speed and PSA thickness were found to be in good agreement. Two different anti-fungal drugs were added to the PSA and the influence of the drug was investigated using contact angle measurements, tensile tests, dynamic mechanical analysis and peel tests.

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Keywords: pressure-sensitive adhesive; peeling; finite element; viscoelastic; cohesive zones; tack; rate-dependent;

1. Introduction

Pressure-sensitive adhesives (PSA) are used in a wide variety of applications including transdermal patches (Venkatraman and Gale 1998, Tan and Pfister 1999, Plaut 2010). The transdermal patches consist of the adhesive and the drug sandwiched between an impermeable backing membrane and a release liner. The research conducted by the authors is aimed at developing a single-layer drug-in-adhesive patch specifically for the human nail with fungal infections. Previously published work has involved characterizing the PSA, backing membrane, PSA-substrate...

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interface and performing peel tests with patches at multiple peel angles, which relates to the force required for removal (Mohammed et al. 2015), as well as modelling the peel test at different speeds and with patches of increasing PSA thicknesses (Mohammed et al. 2016). These factors, directly relate to the pain suffered by the patient upon removal (Chivers 2001) and the drug-loading capacity, respectively. The ultimate aim of the research is to develop a pharmaceutical patch for nails infected with onychomycosis, and this paper focuses on the effect of peeling away the patches when the PSAs are infused with two different anti-fungal drugs, i.e. amorolfine and ciclopirox. Note that polyethylene (PE) was selected as the substrate since it possesses a surface energy similar to that reported for the human fingernail plate (Murdan et al. 2012).

Acrylic-based PSAs are bio-compatible with skin (Tan and Pfister 1999) and unlike rubber and silicone PSAs, do not require the addition of tackifiers to form a good bond with a substrate (Creton 2003). Tack is defined as the ability of a PSA to form an instant bond when it is brought into contact with a surface. The quality of the bond is influenced by numerous factors including the surface energies of the adhesive and substrate, dwell time, contact pressure, mechanical properties of the adhesive, temperature and humidity (Chiang et al. 2010). While tack is necessary to create the bond, it is equally important when a ‘clean’ separation of the surfaces is desirable, such as in the case of drug-loaded patches.

The peel test is a simple experiment in which the force required to separate two surfaces is measured and then used to calculate the energy dissipation (Blackman et al. 2003, Kendall 1975, Moore 2008, Moore and Williams 2010). The magnitude of the resulting peel force depends on variables such as the peeling speed, peel angle, peel arm thickness and adhesive thickness. Modelling of the peeling process accurately is challenging, requiring the material properties of the entire peel arm and a damage criterion to represent the mode of fracture which can be either cohesive or interfacial. Numerous authors have modelled the peel test, using various failure criteria such as the cohesive zone model (CZM) (Blackman et al. 2003, Diehl 2008, Martiny et al. 2008, Williams and Hadavinia 2002), virtual crack closure (Hadavinia et al. 2006), xfem (Sauer 2011) or a critical stress at a distance (Cui et al. 2003, Taylor 2008), but many of these papers simulated a single peeling speed and with relatively thick metallic peel arms bonded using high-modulus structural adhesives.

In the present work, peel tests were performed using specimens which consist of a polyester backing-membrane supporting an acrylic-based PSA (with or without the anti-fungal drugs present) adhered to a PE substrate. Note that the thickness of the PSA layer in this study is comparable to the thickness of the peel arm, unlike the case of structural adhesive bonds where the adhesive layer is often very thin compared to that of the peel arm. The peeling model used a CZM failure criterion and the model has the ability to predict the peel force at different peeling rates.

2. Experimental studies

2.1. Materials

A Scotchpak 9757 backing membrane and DuroTak 2852 PSA were used to make peeling test samples. The backing membrane was a polyester film purchased from 3M while the acrylic PSAs were supplied by Henkel in an organic solvent. The release liner, Scotchpak 9744 from 3M, was a fluoropolymer-coated release liner. When required, two anti-fungal drugs in powder form, i.e. amorolfine and ciclopirox, were dissolved in the PSA, at 5% and 16% by weight respectively, before preparing the samples. The PSAs were then allowed to stand for 24 hours to minimize the formation of bubbles in the samples. The backing and PSA were tested individually and characterized with an elastic-plastic and a visco-hyperelastic material analytical model respectively (Mohammed et al. 2015). A description of the both material models can be found in literature (Goh et al. 2004). In order to perform contact angle testing on the drug-loaded PSAs, four liquids were utilized: water, glycerol, diiodomethane and formamide.

2.2. Tensile properties

Tensile tests were performed on the backing membrane, while both tensile and relaxation tests were performed on the PSA. The backing membrane was found to have an elastic modulus, $E$, and yield stress, $\sigma_y$, of 4.44 GPa and 70 MPa respectively, while the power-law constant, $n$, was calculated to be 0.287. There was a small rate
dependency in the plastic region which was ignored in the present study. The measured thickness of the film was 20μm and the PET surface had a surface energy of 45 mJ/mm². 

The PSA was cast between two fluoropolymer-coated release liners and the solvent was subsequently allowed to evaporate fully to produce a PSA polymer sheet with a thickness of 0.5mm. Samples with a gauge length of 50mm and a width of 10mm were prepared for testing. Tensile tests were performed at true strain rates of 0.1, 1 and 10/min while the relaxation tests were strained to 10 and 100%. The constitutive response of the PSA under step strain relaxation is both strain- and time-dependent. The stress, for any strain history, can be evaluated from the long-term stress-strain relationship corresponding to the instantaneous shear modulus, Ψ, locking stretch constant, λm, and the global interaction parameter, α 

\[
\sigma(t) = g_\infty \sigma_0(t) + \sum_{i=1}^{N} g_i e^{-\frac{t}{\tau_i}} \int_{0}^{\infty} d\sigma(s) ds
\]  

(1)

where \( g(t) \), the time-dependent function, is represented by the Prony series:

\[
g(t) = g_\infty + \sum_{i=1}^{N} g_i \left( \frac{1}{\lambda^i} \right)
\]  

(2)

where \( g_\infty \) and \( g_i \) are dimensionless constants, \( \tau_i \) are the relaxation times and \( g_\infty + \sum g_i = 1 \).

The function \( \sigma_0 \) is calculated through the van der Waals hyperelastic potential with the following material parameters: an instantaneous shear modulus, Ψ, locking stretch constant, λm, and the global interaction parameter, α 

\[
\sigma_0 = \lambda \frac{dW}{d\lambda} = \Psi \lambda \left( \lambda - \frac{1}{\lambda^3} \right) \left[ \frac{\lambda^2 - 3}{\sqrt{\lambda^2 - 3}} - \alpha \frac{\lambda^2 + 2\lambda^{-3} - 3}{2} \right]
\]  

(3)

Therefore, \( \sigma_0(\varepsilon) \) represents the instantaneous stress-strain relationship, corresponding to \( t = 0 \), while \( g_\infty \sigma_0(\varepsilon) \) is the long-term stress-strain relationship corresponding to \( t = \infty \). The hyperelastic constants and Prony series parameters which fit the experimental data for the pure DuroTak 2852 PSA are given in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ψ [MPa]</td>
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<tr>
<td>λm</td>
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<tr>
<td>α</td>
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van der Waals

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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<td>( g_{0.1} )</td>
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</tr>
<tr>
<td>( g_{1} )</td>
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</tr>
<tr>
<td>( g_{10} )</td>
<td>0.099</td>
</tr>
<tr>
<td>( g_{100} )</td>
<td>0.046</td>
</tr>
<tr>
<td>( g_{1000} )</td>
<td>0.038</td>
</tr>
</tbody>
</table>

2.3. Probe tack tests

Poker-chip probe-tack tests were performed on the pure DuroTak 2852 PSA to determine if the interface properties between the PSA and the PE substrate could later be used to represent the traction-separation law of the CZM in the FE modeling. The PSA was cast between two Scotchpak 9744 release-liners. Circular PSA samples of 13 mm diameter were cut from the release-liner/PSA sandwich and subsequently applied to the PE substrate. A 15.6 mm diameter steel probe, attached to a Zwick Roell Z1.0 testing machine, was brought into contact with the PSA surface. The PSA was then compressed to a set dwell force and held for a fixed dwell time before being pulled off at a constant crosshead speed, resulting in failure occurring at the PSA-PE interface. The area under the resulting load-displacement curve was calculated as the tack energy, \( W_{as} \), while the tack strength, \( \sigma_{max} \), was determined by dividing
the peak load by the cross-sectional area of the PSA film. The dwell force and dwell time were both varied between 1–20 N and 10–300 s respectively (Mohammed et al. 2015), in order to determine the minimum threshold value of each variable. The threshold dwell force and dwell time were found to be 10 N and 60 s respectively, and subsequently used in the future probe-tack tests which were performed at pull-off speeds of 1, 10 and 100 mm/min (Mohammed et al. 2016). To determine each threshold parameter, between five to seven replicate tests were performed. Typical stress-time and their corresponding stress-displacement curves at the three pull-off speeds are shown in Fig. 1(a) and Fig. 1(b) respectively.

![Fig. 1. (a) Stress-time and (b) stress-displacement curves for tack tests with pull-off speeds of 1, 10 and 100 mm/min.](image)

### 2.4. Peel tests

Peel test specimens were prepared by casting the acrylic PSAs (with and without the drugs dissolved) onto the Scotchpak 9757 backing membrane and allowing the solvent to evaporate. The release-liner was placed on the PSA to protect its bonding surface and the assembled tape was cut into 15 mm wide and 80 mm long specimens for the peel tests. The release-liner was subsequently removed from the surface of the PSA, the latter having an average thickness of 200μm. Approximately 40 mm of the tape length was then applied to the PE substrate using a roller which ensured that the dwell force was above the threshold value to achieve complete bonding. The free-end of the peel arm was fixed to a tensile grip on a Zwick Roell Z1.0 mechanical testing machine. The PE substrate was attached to a 80 mm × 40 mm IKO precision linear bearing which maintained a constant peel angle during the test.

To investigate the effect of the peel angle employed, experiments with the pure PSA samples were performed at a constant peel crack speed of 100 mm/min and peel angles of 45°, 90° and 135°. At each angle, the peel test was repeated three times. The crack speed was maintained constant for each peel angle by adjusting the crosshead speed appropriately (Moore and Williams 2010). The recorded steady-state peel force decreased as the peel angle increased (Mohammed et al. 2015). Interfacial failure occurred between the PSA and the polyethylene substrate without fibrillation of the Durotak 2852 PSA.

The effect of rate was determined by performing peel tests at a constant peel angle of 90° and constant speeds of 1, 10 and 100 mm/min. At each speed, the peel test was repeated four times and all experiments were performed under environmental conditions of 21 °C and 50% humidity. The results showed that the peel force increased with peeling speed (Mohammed et al. 2016).

### 3. Numerical modeling studies

#### 3.1. The Cohesive zone model (CZM)

Both the probe-tack and peel tests were modeled using the FE software, Abaqus. The backing membrane and the PSA were described by elastic–plastic and visco-hyperelastic material models respectively, with the material
parameters obtained as described in Section 2.2. A rigid body was used to represent the PE substrate and a CZM with a bi-linear traction-separation law was implemented at the PSA-PE interface. The penalty stiffness value, $k$, used was $5 \times 10^{11}$ Pa/m, which was sufficiently high to ensure that the compliance at the interface was negligible. The other two parameters, namely the fracture energy, $G_c$, and maximum stress, $\sigma_{\text{max}}$, were assumed to be equivalent to the experimentally measured tack energy, $W_t$, and tack strength, respectively. This traction-separation curve was used for both normal and shear failure modes. Note that previous simulations showed that the Mode II effect in such peel tests was minimal (Mohammed et al. 2015).

3.2. Probe tack tests

The probe-tack test was simulated with a 2D axisymmetric FE model. The probe, like the substrate, was modeled as an analytical rigid body. A tie-constraint was applied between the probe and the PSA while cohesive contact was implemented at the PSA-PE interface. The substrate was fixed while the probe was given a displacement boundary condition to match the experimental pull-off speeds. As already mentioned, the CZM parameters used were taken from the experimental probe-tack tests (see Section 2.3). A mesh convergence study was performed, from which it was determined that the minimum element size needed was 50μm.

A parametric study was performed to investigate the effect of increasing the PSA thickness, $h_{\text{psa}}$, on the probe-tack test output. The thicknesses simulated varied between 50 and 1500μm, and the output reaction force history was used to calculate the global stress. The simulations showed that the stress–displacement curve closely agreed with the input traction-separation law as the PSA thickness decreases (Mohammed et al. 2016). As the PSA thickness increased, the maximum stress diverged from the input values of $G_c$ and $\sigma_{\text{max}}$ which indicated the influence of the deformation of the PSA on the global response.

Next, the PSA thickness was kept constant and the FE probe was displaced at three pull-off speeds, as was also done experimentally. The CZM parameters used were the values obtained from the probe-tack experiments. These numerical probe-tack results indicated that for a relatively thin PSA film, the rate dependency observed in the probe-tack experiments was due to the rate-dependency of the CZM properties rather than the effect of strain-rate on the deformation of the bulk PSA (Mohammed et al. 2016). This effect was investigated further with peeling simulations.

3.3. Peel tests

A two-dimensional, plane-strain simulation of the peel test was performed using the commercial FE software Abaqus. The entire assembly consisted of two parts: an analytical rigid-body representing the PE substrate and a 2D deformable body for the peel arm, which was then partitioned into the polyester backing membrane and the pure Durotak 2852 PSA adhesive components. The polyester backing membrane and the PSA were modelled using the elastic-plastic and visco-hyperelastic material models, with the parameter given above. A CZM was implemented at the interface between the PSA and the polyethylene substrate, to simulate interfacial failure, as was indeed observed experimentally. The free end of the peel arm was displaced in the required loading direction, while the rigid polyethylene substrate was restrained both horizontally and vertically.

The predicted peel forces from the simulations were in good agreement with the experimentally measured values at various angles and speeds as shown in Fig. 2. Thus the FE model validated both the need for a rate dependent material model for the PSA and the ability of the probe tack test to directly measure CZM parameters. Overall this meant that, with the appropriate input parameters, the peeling FE model could be used to accurately predict the peeling response of drug-load patches.
The predicted peel forces from the simulations were in good agreement with the experimentally measured values. A parametric study was performed to investigate the effect of increasing the PSA thickness, as well as the rate dependency of the CZM properties. It was determined that the minimum element size needed was 50μm.

Table 2. The surface energies and thermodynamic work of adhesion on a PE substrate.

<table>
<thead>
<tr>
<th>An example of a column heading</th>
<th>( \gamma_s^d ) [mJ/mm²]</th>
<th>( \gamma_s^p ) [mJ/mm²]</th>
<th>( \psi_s ) [mJ/mm²]</th>
<th>( \psi_a ) [mJ/mm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DuroTak 2852</td>
<td>29.0</td>
<td>0.8</td>
<td>29.8</td>
<td>67.5</td>
</tr>
<tr>
<td>DuroTak 2852 + ciclopirox</td>
<td>28.3</td>
<td>1.1</td>
<td>29.4</td>
<td>67.0</td>
</tr>
</tbody>
</table>

Table 1 shows the total surface energy calculated with the associated constituent parts: dispersive, \( \gamma_s^d \), and polar, \( \gamma_s^p \). The results show that the addition of the anti-fungal drugs had a minimal influence on the surface energies of the PSAs, which was attributed to the relatively small quantity of drugs infused into the PSA. Furthermore, the thermodynamic work of adhesion, \( \psi_a \), was calculated between the PSAs and PE, and the values are given in Table 1. The thermodynamic work of adhesion between the PSAs and PE was not significantly changed by the addition of drugs to the PSA.

4.2. Tensile tests

Tensile tests were performed at true strain rates of 0.1, 1 and 10/min on DuroTak 2852 PSA samples with 16% wt ciclopirox or 5% wt amorolfine. For clarity, typical tensile stress-strain curves at a single rate for each of the three PSAs, and their associated analytical visco-hyperelastic fits, are shown in Fig. 3(a). The van der Waals hyperelastic constants and Prony series parameters for both PSAs are given in Table 3. As can be seen, the addition of drugs in the PSA had an overall softening effect on the mechanical response.
at different peel angles, peel speeds and PSA thicknesses. The validation of the FE model using the pure PSA softening of the PSA while the surface energy remained relatively unchanged. However, the peel force was

...addition of anti-fungal drugs, ciclopirox and amorolfine. The results showed that the added drug resulted in a global...the CZM to represent the backing membrane, the PSA and the PSA-substrate interface, respectively. 

Fixed-arm peel tests were performed using patches in which the peel arm consisted of a polyester backing membrane supporting an acrylic-based PSA adhered to a PE substrate. Tack tests with a flat steel probe were performed on PSA films adhered to a PE substrate to investigate the interface properties. The measured values of tack strength and tack energy were applied directly into the traction-separation law of the cohesive zone model (CZM) as the maximum stress and fracture energy respectively. Both the peel and tack tests were simulated with the

The predicted peel forces from the FE simulations were in good agreement with experimentally measured values required to remove the patch. The modeling methods described above are currently being applied to the PSAs containing the 16% wt ciclopirox or 5% wt amorolfine drugs to understand the effect of adding these anti-fungal drugs to the measured peel force required to remove the patch.

5. Conclusions

For the specimens with drug-loaded PSAs, peel tests were performed at 100 mm/min and at an angle of 90º. The steady-state forces from the peel tests are recorded in Fig. 3(b) where it can be seen that the peel force was influenced by the added drug: the added 16% wt of ciclopirox resulted in a significantly higher peeling force being required to remove the patch. The modeling methods described above are currently being applied to the PSAs containing the 16% wt ciclopirox or 5% wt amorolfine drugs to understand the effect of adding these anti-fungal drugs to the measured peel force required to remove the patch.

Table 3. The visco-hyperelastic parameters for DuroTak 2852 PSA with ciclopirox and amorolfine.

<table>
<thead>
<tr>
<th>Drug</th>
<th>Ψ [MPa]</th>
<th>λ_m</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ciclopirox</td>
<td>0.078</td>
<td>5.71</td>
<td>0.644</td>
</tr>
<tr>
<td>Amorolfine</td>
<td>0.099</td>
<td>7.01</td>
<td>0.545</td>
</tr>
</tbody>
</table>

Fig. 3. (a) Tensile curves at 10/min and (b) peel force at 100 mm/min for the PSA added with the drugs.

4.3. Peel tests

For the specimens with drug-loaded PSAs, peel tests were performed at 100 mm/min and at an angle of 90º. The steady-state forces from the peel tests are recorded in Fig. 3(b) where it can be seen that the peel force was influenced by the added drug: the added 16% wt of ciclopirox resulted in a significantly higher peeling force being required to remove the patch. The modeling methods described above are currently being applied to the PSAs containing the 16% wt ciclopirox or 5% wt amorolfine drugs to understand the effect of adding these anti-fungal drugs to the measured peel force required to remove the patch.

5. Conclusions

Fixed-arm peel tests were performed using patches in which the peel arm consisted of a polyester backing membrane supporting an acrylic-based PSA adhered to a PE substrate. Tack tests with a flat steel probe were performed on PSA films adhered to a PE substrate to investigate the interface properties. The measured values of tack strength and tack energy were applied directly into the traction-separation law of the cohesive zone model (CZM) as the maximum stress and fracture energy respectively. Both the peel and tack tests were simulated with the finite element (FE) method by implementing an elastic-plastic power law, a visco-hyperelastic material model and the CZM to represent the backing membrane, the PSA and the PSA-substrate interface, respectively.

The predicted peel forces from the FE simulations were in good agreement with experimentally measured values at different peel angles, peel speeds and PSA thicknesses. The validation of the FE model using the pure PSA experimental data offers definitive evidence for the suitability of the FE/CZM approach for modeling fracture of the drug-loaded PSA specimens on various substrates.

Indeed, so far, the bulk PSA has been examined to determine the effect on the mechanical properties due to the addition of anti-fungal drugs, ciclopirox and amorolfine. The results showed that the added drug resulted in a global softening of the PSA while the surface energy remained relatively unchanged. However, the peel force was
influenced by the added drug: the added 16% wt of ciclopirox resulted a significantly higher peeling force being required to remove the patch; and a high peel force is typically associated with an increased ‘pain-level’ being experienced by the patient when the drug-loaded patch is removed. In the future, peel testing and modeling of drug-loaded patches on artificial and human nail beds will be performed.

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