Silicone Release Coatings: A Closer Look at Release Mechanisms

by Glenn V. Gordon
Susan V. Perz
Raymond L. Tabler
Jennifer L. Stasser
Michael J. Owen
James S. Tonge

Dow Corning Corporation
Abstract

The release of a pressure-sensitive adhesive and substrate construction from a silicone-coated liner has many important consumer and industrial applications, from postage stamps to bar code labels. Controlling release-force properties of laminates that consist of a silicone coating, an organic pressure-sensitive adhesive, and substrates that come from a wider range of materials—and doing so in an accurate and consistent way—is of critical importance to Dow Corning Corporation and its customers in the pressure-sensitive adhesive industry.

The mechanism of releasing the liner is an extremely complex dynamic process assumed to be based on adhesion, interfacial energy, surface topography, and rheology. The study described in this paper was conducted to improve fundamental understanding of the primary contributions of the laminate construction components to the release mechanism. Data analyzed from this study, which focused on solventless release coatings containing various levels of high-release additive, will serve as a guide to future development of silicone release coating technology.
Introduction

Silicone release liners are associated with a variety of common products including diaper tabs, bar code labels, packaging tapes, and postage stamps. In its simplest form, a release coating is a liquid or solid that forms a weak boundary layer between two potentially interacting substrates—for example, between cookie dough and a baking pan, or between barnacles and a ship’s hull. This boundary layer prevents intimate contact and the resulting development of adhesive strength. Any transfer of release agent should not hinder use of the separated surfaces.

This paper deals with pressure-sensitive adhesive (PSA) applications, in which no transfer—or, at most, very little transfer—of release agent is desired. In this application, the migration (or offset) of release agent would prevent the adhesive from developing its potential bond strength with its ultimate end-use adherend such as paper, metal, glass, or textile. The adhesive and the substrate to which it is attached represent the functional materials; the release liner is merely the device by which to protect and aid delivery of the PSA.

Literature reports on PSAs generally address the peel testing of adhesives at high peel forces and low peel speeds, and they highlight adhesive, cohesive, or chaotic adhesive/cohesive failure mechanisms [1]. Release coatings, by design, always fail adhesively and release at much lower peel forces. The most dominant technology in industry is based on polydimethylsiloxane (PDMS), which holds a unique position among release surfaces. Until recently most of the published literature on release coatings has dealt with the cure mechanism by which release coatings are produced [2–5], the temperature dependence of viscoelastic properties [6], or a general overview [4, 7]. The recent renaissance in adhesion mechanism studies [8–13], and the maturation of nanoscopic tools [14, 15] capable of probing individual polymer chains at interfaces, have led to the macroscopic and nanoscopic reexamination of silicone release coatings. Investigative work of this nature has helped researchers broaden their understanding of the release mechanism of the adhesive/substrate construction [16–18].

The construction process for PSAs involves an initial bonding stage as the cured silicone coating and adhesive are joined, followed by a debonding step at the time of use. The interval in which these two events transpire may be relatively short (as to incompletely wet the adhesive), or may be separated by significantly longer periods of time. The rate at which delamination occurs also may vary over several orders of magnitude. For example, it can depend on whether an individual is slowly peeling a tape, or a machine is applying labels automatically at high speed. These factors, combined with process variables (e.g., extent of cure, relative humidity, temperature, and choice of materials for the substrates) add to the complexity of designing a controlled release surface. This study arose from an underlying need to address some of the variables and to model the processes contributing to the release mechanism of PSAs.

Peel testing is typically analyzed in terms of a systems approach based on a universal thermodynamic energy balance. The energy required to peel an adhesively bonded material from its substrate is a direct measure of interfacial adhesion if no energy dissipation occurs because the laminate components are elastic. At the atomic level, this work of adhesion can be classified by three general mechanisms: (1) formation of direct chemical bonds, as promoted by reactive functionality such as silane coupling agents; (2) diffusive interpenetration of polymer chains across the interface and coupling by chain entanglement; and (3) van der Waals forces or other weak interactions. The third mechanism is unavoidable but PDMS, by virtue of its low surface energy and incompatibility with organics, minimizes or eliminates contributions from mechanisms 1 and 2.

Although silicones and fluorocarbons have low surface energies, 25 years of concerted effort have shown that fluorocarbons are of little utility in PSA applications. Thus, surface energy alone is not totally responsible for adhesion control. The actual work of separation is always higher than that predicted from a knowledge of surface energies of the adhesive and the adherend, due to the mechanical dissipation phenomenon that occurs during the separation. When an external force is applied, complicated stress and strain distributions will be generated within the laminate construction, including the interface, adhesive layer, and release coating. The energy of peeling partitions into energy dissipation in the form of heat and an internal energy change. The mechanical work done during peeling that is not dissipated as heat is effectively stored in the laminate components or is consumed in creating the surfaces exposed by peeling. Only a fraction of the total energy of peeling is involved in internal dissipative processes and, of this fraction, a smaller percentage is involved in the reversible work of adhesion between adhesive and adherend [19]. Identifying the modes of dissipation with specific molecular motions will enhance our understanding of the structure-property relationship for release coatings and allow the degree of release control desired by the PSA industry.

Newby and co-workers [20] proposed that local viscous energy dissipation was substantial at the developing crack tip, and that the local slip reduced this dissipation. Slip concentrates shear forces at the interface, resulting in low release forces. A high degree of slippage, or low friction, is cited as the predominant reason PDMS has lower release forces than the lower surface energy, but higher friction, fluorocarbon polymers. The Newby study alluded to one part of the release puzzle. Further definition of how to controllably increase release force without inducing release instability due to mechanisms 1 and 2 cited above has yet to be determined.

Solventless systems account for approximately two-thirds of the current market in release coatings and dominate the labeling industry which, in turn, represents approximately 70% of the pressure-sensitive market volume. However, compared to solvent-based and emulsion systems, tight release
properties are the most difficult to control. Functioning as a major component in a high-release additive (HRA), siloxane resins are incorporated into the silicone network to modify and control release, although the resulting effect on the release mechanism is not clearly understood [4, 18, 21]. The object of this study was to define other pieces of this puzzle—specifically, the contribution from the work of adhesion and the energy dissipative properties—for HRA-modified solventless silicone release coatings with two representative adhesive technologies.

**Experimental Materials**

Solventless silicone coating systems containing varying levels of HRA were prepared via addition-cure chemistry [4]. Test specimens 1.5 μm in thickness were cured onto 54.5-lb Nicolet SCK paper at 205 °C for six seconds and used as liners in peel tests. For surface analyses, specimens were coated either to a 1.5 μm thickness on Mylar sheets (51 μm thick) at 177 °C with a dwell time of 20 seconds, or to a 75 μm thickness on silicon wafers (0.5 mm thick) at 120 °C with a dwell time of 10 minutes. For rheological characterization, release coating samples from 1.3 to 1.6 mm in thickness were cross-linked in situ between 8-mm diameter parallel-plate test fixtures at 130 °C for over three hours. This approach allowed real-time monitoring of the extent of cure and, more importantly, ensured intimate contact between the test fixtures. Industry standard tapes for determining the performance characteristics of release liners were selected to represent two major adhesive technologies: the tesa® 7475 acrylic- and 7476 rubber-based adhesives with PVC and cloth substrates, respectively. A Solutta Gelvam® RA-1753 acrylic adhesive also was employed for comparative purposes.

**Measurements**

Peel testing to profile release force as a function of peel rates (from 5.08 to 5080 mm·s⁻¹) was conducted with Instrumentors 3M90 Slip/Peel and ZPE-1000 High-Rate Peel Testers. Tests were performed using a 180° peel angle at ambient conditions with 25.4-mm wide laminates aged for a day at room temperature. The thickness of each PSA tape component was measured using scanning electron microscopy (JEOL JSM-6100). Analysis of surface topography as a function of HRA concentration was carried out using several techniques: a Tencor P-10 Surface Profiler that used a 5-μm radius-of-curvature diamond stylus with a 0.5 μN force over a specimen length of 1 mm and at scanning and sampling rates of 20 μm·s⁻¹ and 100 Hz, respectively; a Digital Instruments Dimension™ 5000 scanning probe microscope in which atomic force micrographs were acquired in TappingMode™ with a silicon probe tip oscillating at resonance (200 kHz) with a 0.1 nm vertical and a 1-5 nm lateral resolution over a 2 × 2 μm² area; and a Zygo Maxim 3D Phase Measurement Interference Microscope, which combines optical microscopy with laser interferometry to obtain noncontact three-dimensional topographical measurements with 0.1 nm height resolution over a 0.25 × 0.25 mm² field of view. Surface energy and static contact angle measurements were obtained from an AST VCA-2000 Video Contact Angle System, whereas a Rame-Hart Model A-100 goniometer was used to study dynamic contact angle hysteresis. Surface energy information was obtained by applying the Owens-Wendt/Young equation [22] to contact angle measurements with water, methylene iodide, and hexadecane; and via a contact mechanics approach according to the Johnson–Kendall–Roberts theory [23] using a custom-built apparatus courtesy of M. K. Chaudhury and Lehigh University. To access the frequencies corresponding to the peel rates, isothermal, frequency-sweep rheological experiments were performed in shear deformation within the linear viscoelastic region using Rheometric Scientific™ RDSII and RDAII dynamic mechanical spectrometers from 30 °C to below the glass transition temperature.

**Results and Discussion**

**Release Profiles**

Figure 1 illustrates the release force profiles for solventless silicone-coated liners peeled at a 180° angle at ambient conditions from two different PSA tapes.

![Logarithmic plot of release force as a function of peel rate for 25.4-mm wide laminate constructions at ambient conditions.](image)

At a constant peel rate, release force increased with HRA concentration. However, the incremental modification in release force with HRA concentration was not independent of the peel rate. Moreover, contrasting release profiles were obtained between the tesa® 7475 acrylic- and tesa® 7476 rubber-based adhesives over the applied range of peel rates. For the acrylic-based adhesive, release force steadily increased, seemingly independent of...
the HRA concentration, at rates below $10^3$ mm·s$^{-1}$ prior to displaying a maximum at approximately $10^{1.2}$ mm·s$^{-1}$. After this point a slight decrease in release force was apparent. For the rubber-based adhesive, release force did not vary considerably at low peel rates. At a constant HRA concentration within this range of peel rates, the release force was significantly greater than that obtained from the acrylic-based tape. Above 400 mm·s$^{-1}$, the rate dependence of release force exhibited a decreasing profile. For peel rates above $10^3$ mm·s$^{-1}$, the release force from the rubber-based adhesive was significantly lower compared to that obtained from the acrylic adhesive.

Given the same PDMS polymer network, release can be further controlled by altering the HRA composition. Figure 2 shows a typical result where, at low to intermediate peel rates, release was significantly modified. The HRA concentrations in PDMS were formulated so the amount of siloxane resin in each of the four HRA-modified release systems was equivalent (as represented by an identical symbol) relative to that shown in Figure 1. However, the release profiles from each PSA tape were relatively unaffected by the change in HRA composition.

![Graph](image)

**Figure 2.** Logarithmic plot of release force as a function of peel rate for 25.4-mm wide laminate constructions at ambient conditions. Relative to Figure 1, release at low to intermediate peel rates can be tailored by adjusting the HRA composition. The HRA concentrations in PDMS were formulated so the amount of siloxane resin in each of the four HRA-modified release systems was equivalent—by comparing identical (filled or unfilled) symbols—to those shown in Figure 1.

Under the assumption that the release profiles shown in Figures 1 and 2 are governed by adhesive failure, the two primary contributions to the release mechanism would be from the thermodynamic work of adhesion (intrinsic surface energy) and from the viscoelastic response from the non-rigid components of the laminate construction [11, 24, 25]. The first contribution, which represents the energy required to separate an interface reversibly and hence does not depend on the separation rate, dominates the nanoscopic regime where molecular interactions are significant. Adhesive failure energy $G_a$ can be derived from the measured release force per unit width $F_R$ and the peel angle $\theta$ by the relation [26]

$$G_a = (1 - \cos \theta) F_R$$  \hspace{1cm} (1)

For a $180^\circ$ peel angle used in this study, Equation (1) reduces to

$$G_a = 2F_R$$  \hspace{1cm} (2)

However, the measured works of adhesion required to overcome interfacial energetics are typically on the order of $10^2$ to $10^3$ N·m$^{-1}$ and, for example, cannot begin to account for the range of experimentally observed release forces in Figures 1 and 2, which are on the order of $10^0$ to $10^2$ N·m$^{-1}$. From adhesion measurements, Andrews and Kinloch [27] rationalized the discrepancy by introducing a threshold energy factor; however, its origins have not been firmly demonstrated [28–30]. In light of the release profiles shown in Figures 1 and 2 in which release force did not fall below 3 N·m$^{-1}$ regardless of the peel rate, the concept of a threshold energy seemed plausible.

The second contribution reflects primarily the energy dissipated irreversibly within the bulk of the viscoelastic material(s) in the laminate construction. A generalized dissipation function with respect to adhesive failure has not been established [11] although an empirical power-law form taking into account its rate dependence has been reported elsewhere [31, 32]. Energy dissipation can also occur at the interface. Newby and Chaudhury [33] calculated that energy dissipative frictional processes can range from $10^1$ to $10^2$ N·m$^{-1}$; however, interfacial slippage can be extensive for PDMS, thereby reducing the interfacial energy dissipation [12, 20].

**Work of Adhesion**

A popular hypothesis regarding the role of the HRA relates to the modification of surface energy: the increase in release force at a given peel rate is due to an increase in the work of adhesion [21]. A contact mechanical approach based on the Johnson–Kendall–Roberts (JKR) theory [23] is currently used for the direct estimation of the work of adhesion and thus the surface free energy. The radius of a contact area generated between an elastic spherical surface and a flat surface compressed by a normal force $P$ is described by the equation

$$a^3 = \frac{R}{K} \left\{ P + 3\pi GR + \left[ 6\pi GRP + (3\pi GR)^2 \right]^{1/2} \right\}$$  \hspace{1cm} (3)

where $R$ is the radius of curvature of the sphere, $K$ is the elastic constant, and $G$ is the energy release rate. If thermodynamic equilibrium conditions established by the initial contact of the surfaces are sustained over the course of the JKR experiment, the measured energy release rate during the loading stage $G_a$ corresponds to the work of adhesion. In self-adhesion experiments, where both surfaces in contact
are identical, the work of adhesion is just twice the surface free energy. Figure 3 plots the results for $G_L$ as a function of the weight fraction of HRA for the release coating system depicted in Figure 1. The inset shows the loading curves, where the intercept and slope of each line is $-(G_L K)^{1/2}$ and $K$, respectively.

![Figure 3](image_url)

**Figure 3.** Energy release rate as a function of the concentration of high-release additive in the silicone release coating. Error bars represent the estimated standard errors. The inset shows data sets obtained from the 1 mN•s⁻¹ loading stage of self-adhesion JKR experiments at ambient conditions. The intercept and slope of each line is $-(G_L K)^{1/2}$ and $K$, respectively.

The elastic constant increased quadratically with HRA concentration from 5.02 ± 0.62 to 11.0 ± 0.2 MPa. For the unmodified PDMS coating, an experimentally observed $G_L$ of 44.2 ± 0.8 mN•m⁻¹ was consistent with the range of surface energies cited for PDMS in the literature [34]. The works of adhesion between the unmodified coating and the adhesives were observed to be 49.2 ± 7.0 and 18.9 ± 3.7 mN•m⁻¹ for the tesal® 7475 acrylic- and tesal® 7476 rubber-based PSA tapes, respectively.

In the self-adhesion experiments, an initial increase in adhesion energy was observed at the lowest HRA concentration. However, as the HRA concentration in the release coating increased, the work of adhesion decreased, eventually to 41.3 ± 1.2 mN•m⁻¹ at 80 wt% HRA—a trend that was found to be reproducible. The observed decrease in the work of adhesion with increasing HRA content may, in part, be explained by the siloxane resin structure. This structure is essentially composed of core silicate $(SiO_{2n})$ clusters surrounded by a shell of trimethylsiloxy groups, thereby leading to lower surface energies in the silicone coating. Amouroux and Léger [18] also observed an apparent decrease in $G_L$ with siloxane resin concentration. However, they illustrated that by accounting for kinetic effects, the work of adhesion between PDMS and an acrylic adhesive slightly increased from 46.5 mN•m⁻¹ for the unmodified silicone to 50 ± 5 mN•m⁻¹ for the silicone containing 40 wt% resin. Regardless of the trend depicted in Figure 3, it is more important to realize that the variance in the work of adhesion due to the incorporation of HRA did not exceed 0.005 N•m⁻¹, whereas the resulting modifications in release force were on the order of 10 N•m⁻¹.

The JKR experiment was conducted in two stages: the loading and unloading of the normal force $P$. The energy release rate obtained from the latter stage is typically larger because of the additional contribution from a number of chemical and mechanical factors. These factors, which may or may not be coupled, may include the reorganization of molecular groups at the interfaces that has been described as interdiffusion, interdigitation, interpenetration, or reptation [35, 36], surface roughness and heterogeneity, energy dissipation, and viscoelastic deformation [37]. Hysteretic behavior is also observed in either static or dynamic contact (between advancing and receding) angle measurements with water. The hysteresis in the measurement of PDMS-based systems has been reported by several authors [38–41] and was attributed to partial reorganization of the surface in response to the polar nature of the test solutions. It was proposed that polar groups such as residual silanol groups were drawn to the surface to reduce the interfacial tension with water and other polar media, with the degree and time frame of such reorganization being system dependent.

![Figure 4](image_url)

**Figure 4.** Effect of the concentration of high-release additive in a solventless silicone release coating on adhesion and contact angle hysteresis. Hysteretic behavior was observed from the JKR self-adhesion experiments (loading and unloading) and from the static and dynamic contact angle (advancing and receding) measurements with water at ambient conditions.

In such a scenario, the HRA-modified release coatings would be anticipated to have lower hysteresis due to an increased stiffness. In spite of the nonmonotonic trend observed in the adhesion hysteresis from the JKR experiments, Figure 4 does not provide sufficient evidence for such a scenario. In contrast, the other two sets of results plotted in Figure 4 indicate that the level of contact hysteresis from both static ($r = 0.90, p = 0.036$) and dynamic ($r = 0.99, p = 0.001$) measurements with water increased linearly with HRA content.
Surface energy increased with HRA concentration from 19.7 ± 3.8 to 25.5 ± 3.1 mN·m⁻¹, with the apparent increase primarily from dispersion forces. However, if weighted by the inverse of the estimated standard variance, the linear association shown in Figure 5 was still significant within 5% error (r = 0.83, p = 0.08). Comparing results from the two techniques and taking into account the estimated standard errors, no substantial difference was found among the release coatings containing up to 40 wt% HRA. However, a distinction was evident at the two highest HRA loadings. From another conceptual perspective, it has been proposed that the role of the HRA in release modification is one in which the resin partitions to the surface, causing surface roughness and thereby providing some explanation for the hysteretic behavior. Surface roughness can decrease the contact area in a contact mechanics experiment leading to an apparently lower surface energy [35]. In part, this may explain the discrepancy between the two techniques at the higher HRA concentrations.

Release modification caused by HRA was also thought to be a physical phenomenon, produced by an increase in the area of interaction between the release liner and the adhesive. Stein and co-workers [21] addressed this problem using secondary ion mass spectrometry analysis of model resin-filled release coatings. They found no evidence for concentration gradients at the interface to support the thesis. An electron spectroscopy for chemical analysis (ESCA) of the system used in this study observed only gross bulk compositional changes at the higher HRA loadings; that is, the resolution from ESCA could not distinguish if siloxane resin was partitioned at the interface.

To further interpret the contribution of the HRA to the release mechanism, atomic force microscopy (AFM), phase-measurement interference contrast microscopy, and profilometry were used to characterize the surface topographies for the release coating system in Figure 1. Figure 6 displays typical 2 × 2 μm² TappingMode™ AFM images using silicon wafer as a substrate. Scanning electron microscopy and wider area AFM image scans confirmed the uniformity of the coatings on the substrates. Subsequent experimental data revealed that a standard deviation of 0.006 nm in roughness can be expected for 2 × 2 μm² uniform surfaces exhibiting sub-nanometer roughness. The arithmetic average
(R_a) and root-mean-square (rms) roughness increased linearly from 0.40 to 0.53 nm and from 0.50 to 0.66 nm, respectively, with 86% of the variability in surface roughness accounted for by the concentration of HRA in the release coating.

Figure 7 shows noncontact three-dimensional surface scans from phase-measurement interference microscopy using Mylar™ as a substrate. Whereas the silicon wafers used in the AFM experiment had an approximate roughness of 0.2 nm, Mylar™ had an average roughness of 40 nm. The arithmetic average and rms roughnesses ranged from 3.1 ± 0.2 to 5.7 ± 0.8 nm and from 4.2 ± 0.3 to 7.8 ± 0.9 nm, respectively. In contrast to the AFM technique, the relationship between surface roughness and HRA concentration was nonmonotonic and may be due to a substrate effect.

Figure 8 compares the results from the three techniques. The surface roughness measurements were found to be dependent on the specimen area being scanned. The resolution from the noncontact technique (phase-measurement interference microscopy) was an order of magnitude greater than that using contact-type measurements. From two-dimensional profilometry and using silicon wafers as substrates, an average roughness of 0.93 ± 0.05 nm (rms = 1.14 ± 0.07 nm) was obtained for the unmodified release coating. The effect of HRA content on the average and rms roughness was nonmonotonic. Hence, the trends from profilometry and phase-measurement interference microscopy appeared to be qualitatively consistent with the greatest change in surface roughness occurring at the highest HRA concentration. Interestingly enough, the nonmonotonic behavior in surface roughness from these two techniques was reminiscent of the adhesion hysteresis obtained from JKR experiments (Figure 4).

**Viscoelastic Functions**

To relate the linear viscoelastic properties to the release profile, time–temperature superposition [42] was applied. This principle effectively extends the frequency range inaccessible by rheological instruments to correspond to the delamination rates in the peel test. For the dynamic shear modulus G*, the correspondence between time (ω⁻¹) and temperature T is expressed as

\[
\frac{G^{*}(T, \omega)}{\rho(T)T} = \frac{G^{*}(T_{R}, \omega_{R})}{\rho(T_{R})T_{R}}
\]

where \( \omega_{R} \) is a material-dependent shift factor along the frequency axis based on a reference temperature \( T_{R} \). A slight vertical shift along the ordinate axis results from the inherent temperature dependencies of density \( \rho \) and modulus. The dynamic frequency \( \omega \) can be related to the rate of delamination \( \nu \) by accounting for the thickness \( h \) of the material subject to deformation in the peel test.
Figure 9 shows the rheological master curves for the HRA-modified release coatings shown in Figure 1 at a reference temperature of 25 °C. The HRA functions to increase the storage modulus \( G' \), due to the elastic character of the siloxane resin, and, to a greater extent, the loss modulus \( G'' \) by disrupting the network formation of PDMS. The dotted line brackets the frequency range corresponding to the rates used in peel testing based on a nominal coating thickness of 1.5 \( \mu m \).

\[
\omega = \frac{2\pi}{h} v
\]  

Figure 9. Rheological master curves for the HRA-modified release coatings shown in Figure 1 at a reference temperature of 25 °C. The HRA functions to increase the storage modulus \( G' \), due to the elastic character of the siloxane resin, and, to a greater extent, the loss modulus \( G'' \) by disrupting the network formation of PDMS. The dotted line brackets the frequency range corresponding to the rates used in peel testing based on a nominal coating thickness of 1.5 \( \mu m \).

\( G' \) can be decomposed into an elastic modulus component \( G' \) and a loss modulus component \( G'' \). The latter is directly proportional to energy dissipation [43]. The horizontal shifts to a reference temperature of 25 °C were based on \( G'' \), whereas the temperature dependence of modulus accounted for the vertical shifts. Results indicate that the HRA functions to increase the storage modulus \( G' \), due to the elastic character of the siloxane resin, and, to a greater extent, the loss modulus \( G'' \) by, at least in part, perturbing the ideal network formation of PDMS. Based on \( G' \), the cross-link modulus at 25 °C increased quadratically from 1.2 MPa for the unmodified silicone release coating to 3.6 MPa for the release coating with 80 wt% of HRA. This increase was in a manner consistent to that observed for the elastic constant \( K \) from the JKR experiments. However, it is the effect on \( G'' \), which in essence enhances the total energy-dissipating character of the laminate construction, that provides, at the very least, one qualitative explanation for the role of the HRA in modifying release force. The systematic increase in viscoelasticity may also be related to the linear trend observed for the hysteretic behavior from contact angle measurements depicted in Figure 4. This was not unexpected given that hysteretic behavior is an inherently dissipative phenomenon.

Figure 9 also shows the dynamic loss tangent, which, by definition \( \tan \delta = \frac{G''}{G'} \), describes the relative ability of a material to dissipate and store energy at a particular frequency. From Equation 6, the frequency window corresponding to the range of peel rates in Figure 1 is between \( 2.1 \times 10^4 \) to \( 2.1 \times 10^7 \) rad s\(^{-1} \) for a nominal coating thickness of 1.5 \( \mu m \). However, within this window, all three rheological functions increase with frequency and cannot rationalize the release-force profile exhibited by the release system using the rubber-based adhesive, which essentially decreases at the intermediate to high peel rates.

Figure 10 shows the rheological functions for the tesa\(^*\) 7475 acrylic-based and tesa\(^*\) 7476 rubber-based adhesives at 25 °C.

\[
\tan \delta = 2 \pi \frac{G''}{G'}
\]

Figure 10. Rheological master curves for the tesa\(^*\) 7475 acrylic-based and tesa\(^*\) 7476 rubber-based adhesives at a reference temperature of 25 °C. From Equation 6, the dotted lines delineate the frequency windows corresponding to the peel rates shown in Figures 1 and 2 and the thickness of each adhesive in the tesa\(^*\) tape construction as measured from scanning electron microscopy.

Except for \( \tan \delta \), these are scaled for comparison to the release-coating properties in Figure 9. For the adhesives, the \( \tan \delta \) scale is quadrupled, further emphasizing their energy-dissipating capability compared to the release coating, which remains primarily elastic throughout the frequency range of interest. The viscoelastic profiles are differentiated by the position and breadth of the loss tangent: the acrylic- and rubber-based adhesives were characterized by \( \tan \delta \) peaks at frequencies of \( 10^5 \) and \( 10^7 \) rad s\(^{-1} \) with breadths of 2.23 ± 0.06 and 1.30 ± 0.03 decades, respectively.
Figure 10 also delineates the frequency windows for the acrylic (h = 82 μm) and the rubber (h = 40 μm) adhesives corresponding to the rates used in peel testing. These data were based on the measured thickness of each component in the PSA tape construction via scanning electron microscopy. The position of each frequency window, being far removed from the terminal flow regime, ruled out cohesive failure within the adhesive layer. This validated the assumption that the release mechanism is governed by adhesive, or interfacial, failure. Within each window, it was apparent that the frequency dependence of tan δ correlated with the release profiles. The positions of the tan δ maxima within the frequency window appeared responsible for the high- and low-rate peel behavior of the acrylic- and rubber-based systems, respectively, in which release force apparently exhibited a maximum (Figure 1).

With the realization that several factors affect release performance [4], a linear correlation (r = 0.81, p = 0.004) between the logarithm of release force for the unmodified silicone-coated liner and the logarithm of tan δ(ω, h) of the adhesive was satisfactory (Figure 11).

Being highly elastic, the unmodified PDMS network, the paper release liner, and both types of adhesive substrates used in this study can be assumed to be unable to significantly dissipate energy within the frequency range of interest. Therefore, the energy-dissipative contribution from the adhesive to the release force $F_h$ (N·m⁻¹) at a given peel rate within the regime of testing (5.1–5080 mm·s⁻¹) can be expressed as a power-law function

$$ F_h(ν) = 5.81(±0.59) \left[ \tan δ(ω, h) \right]^{0.04 ± 0.19} \tag{7} $$

where $\tan δ$ is a function of effective debonding frequency $ω$ as defined by the adhesive thickness $h$ and peel rate $ν$ in Equation 6. The relationship between $\tan δ$ and release force is significant for two reasons: $\tan δ$ is not dependent on the geometry of the material element being deformed, nor is it dependent on the type of deformation occurring during the peeling process. In analyzing the peeling of flexible laminates, Kinloch and co-workers [44] considered the adhesive failure energy to be a geometry-independent parameter. The coefficient in Equation 7 does not appear to be dependent on the work of adhesion as suggested in the literature [11, 23, 45]. As an adhesive becomes more elastic, $\tan δ$ decreases, thereby reducing its energy-dissipative contribution to release force. To illustrate further, if $\tan δ$ were on the order of $10^{-4}$ at the frequency corresponding to a particular peel rate, the adhesive component would essentially respond elastically—like the other three components of the laminate construction—to the application of force. From Equation 7, the resulting contribution to release force, on the order of $10^{-2}$ N·m⁻¹, would then be comparable or even less than that expected from the work of adhesion. Hence, Equation 7 is consistent with the energy balance for an adhesive failure mechanism.

The modification of release force with increasing HRA concentration can also be rationalized in terms of the increase in the energy-dissipative function of the release coating. From Figure 9, it was apparent that the frequency dependence of both $G''$ and $\tan δ$ were affected by the incorporation of HRA, which may help explain an earlier observation that incremental modification in release force with HRA concentration was seemingly dependent on the peel rate. Prior to modeling the effect of the HRA, it was important to realize that being of lower surface energy compared to the organic adhesive, it is incumbent on the silicone component in a release system to wet the surface of the adhesive and create a weak boundary layer. The kinetic aspect of this controlled adhesion process can be related to the creep compliance as proposed by Yang [46]. For highly elastic materials ($\tan δ < 1$) such as the solventless release coatings, the creep compliance can be approximated by the reciprocal of the storage modulus at the bonding frequency, $G''(ω_b)^{-1}$. For the peel test specimens aged for at least a day, the corresponding bonding frequency therefore is on the order of $10^{10}$ s⁻¹. Based on their master curves (for example, see Figure 9), the crosslink modulus for each of the release coatings can be effectively considered as $G''(ω_b)^{-1}$. Using the loss modulus to represent the energy-dissipative contribution to the release mechanism, the role of the HRA in the release mechanism takes the empirical form

$$ \Delta F_h(ν) = β_h \left[ G''(ω, h) / G''(ω_b) \right]^{β_1} \tag{8} $$

where $ΔF_h(ν)$ is the change, or modification, in release
force due to the incorporation of HRA into the elastic silicone network at a given peel rate $\nu$, $G'(\omega, h)$ is a function of the frequency corresponding to the peel rate and thickness of the release coating, and $\beta_1$ are empirical fitting parameters. Figures 12 and 13 plot the change in release force, due to the incorporation of HRA, as a function of the viscoelastic function contribution from the release coating for the acrylic- and rubber-based adhesives, respectively.

The analysis was partitioned as a function of peel rate because of the significant influence of the adhesive on release force. If the role of the HRA in the release mechanism is solely due to a viscoelastic modification in the release coating, the scaling exponent $\beta_1$ should be independent of the type of adhesive forming the interface with the silicone. There is insufficient evidence to reject the hypothesis that there is no difference in the mean values for $\beta_1$ ($p = 0.52$) obtained from each adhesive. Therefore, the average contribution of the HRA to the release mechanism for the solventless release coating system used in this work may be represented as

$$\Delta F_r(\nu) = 22.7(\pm 6.0) \left[\frac{G''(\omega, h)}{G'(\omega, h)}\right]^{0.41 \pm 0.01} \quad (9)$$

**Effect of Adhesive Thickness on the Release Profile**

The results presented here suggest that the adhesive dictates the release profile because of its energy-dissipating capability relative to the other components in the release system. This hypothesis was tested by using the Solutia Gelva® RA–1753 acrylic adhesive, which was characterized and found to exhibit viscoelastic properties similar to the tesa® 7475 adhesive (Figure 14).

The RA–1753 was laminated onto either a Mylar™ or stainless steel substrate to a nominal thickness of 24 $\mu$m. As shown in Figure 14, the effect of decreasing the adhesive thickness is to shift to higher frequencies the window corresponding to the range of delamination rates used in peel testing, calculated from Equation 6, is based on an adhesive thickness of 24 $\mu$m.
The data also show that neither of the elastic adhesive substrates contributed substantially to the energy dissipation process. Hence, different release profiles can be obtained by simply varying the adhesive thickness with prior knowledge of the linear viscoelastic properties. Also noteworthy, when comparing the release profile for the tesa® 7475 acrylic adhesive/PVC substrate in Figure 1 with the Gelva® RA–1753 acrylic adhesive in Figure 15, is that the maximum release force observed for each release coating was comparable in magnitude even though the adhesive thickness varied by more than a factor of 3.

**Summary**

The release mechanism of an organic pressure-sensitive adhesive and substrate construction from a solventless silicone-coated liner is controlled by adhesive failure that, in turn, is a summation of the contributions from the work of adhesion and the rheological properties of the laminate construction. The release profile is dictated by the adhesive component and its relative ability to dissipate and store energy as defined by the dynamic loss tangent function derived from linear viscoelastic measurements. On the other hand, the magnitude of release force can be further amplified by the introduction of high-release additives based on siloxane resins, which function primarily to enhance the energy-dissipative capability of the entire release system. The measured changes in the work of adhesion with the incorporation of HRA were on the order of $10^{-3}$ to $10^{-2}$ N·m$^{-1}$ and together with surface topography played significantly lesser roles in the modification of release forces, which were in the range of $10^0$ to $10^2$ N·m$^{-1}$.

**Acknowledgments**

Support of this interdisciplinary research was provided by C. J. Bilgrien, J. D. Jones, and R. G. Schmidt (Dow Corning Corporation). The authors also wish to acknowledge the Center for Interfacial Engineering at the University of Minnesota for the use of the profilometry and phase-measurement interference microscopy equipment, M. K. Chaudhury and H. She for the JKR and dynamic contact angle measurements performed at Lehigh University, and D. Ahn for helpful insights.
References


