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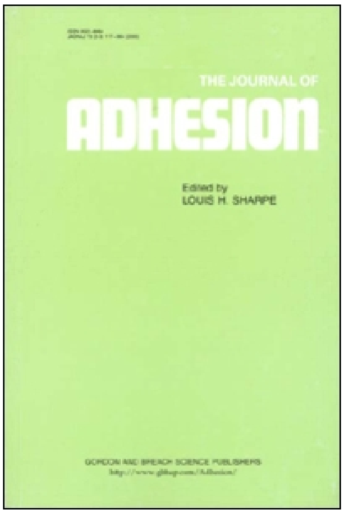

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PSA Release Force Profiles from Silicone Liners: Probing Viscoelastic Contributions from Release System Components*

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Release force profiles of an acrylic- and rubber-based pressure sensitive adhesive (PSA) from silicone release coatings containing different levels of a high-release additive (HRA) were measured. The profiles of release force differed dramatically for the two different adhesive types. The general trends of either increasing or decreasing release force profiles with peel rate were predominantly attributed to the relative ability of the adhesive component to dissipate and store energy (*i.e.*, tan δ) over the operating frequency range. The addition of HRA enhanced the dissipative character (G'' and tan δ increased) of the release coating which resulted in higher release forces. An empirical model based on the viscoelastic properties of the adhesive and release coating was proposed to describe release force profiles and initial estimates for the fitting parameters were determined. The release model was shown to predict successfully the impact of adhesive thickness on the release force profile using an acrylic PSA which was not used for the model development. Some evidence was also obtained for the validity in omitting the contributions of the elastic backing components from the model.

Keywords: Silicone release coatings; viscoelastic properties; adhesion model; release force model; high-release additive; pressure sensitive adhesive

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1. INTRODUCTION

A silicone liner is commonly used to release an organic pressure sensitive adhesive (PSA) before the adhesive label, wrap or tape is placed in its final position. In PSA applications, no transfer – or, at most, very little transfer – of the release coating is desired. In these applications, the migration (or offset) of release agent can 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 a device to protect and aid delivery of the PSA. The release system typically consists of four components: a release liner coating which is in direct contact with a PSA, with each being supported by a backing. From a scanning electron micrograph of the cross-section of the release system (Fig. 1), it is apparent that the silicone release coating is by far the thinnest component (on the order of 1 – 2 μm) compared with the 40 – 300 μm thickness range for the PSA and the two backing components.

The construction of a PSA/release liner system involves an initial bonding stage as the cured silicone coating and organic adhesive are laminated, followed by a peel debonding step immediately prior to applying the PSA. The interval in which these two events transpire

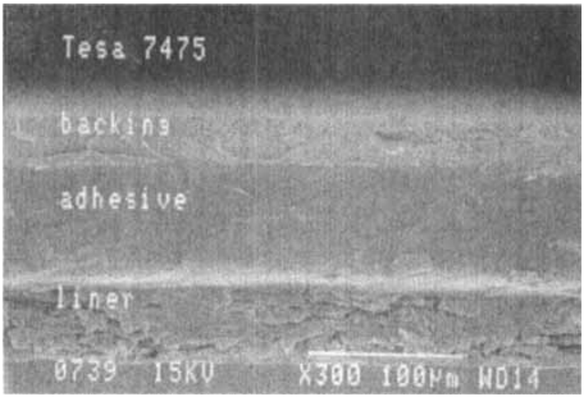

FIGURE 1 Scanning electron micrograph of release system cross-section based on tesa® 7475 acrylic adhesive (~80 μm), PVC backing for PSA (~40 μm), silicone coating (~1.5 μm) and a paper backing (~60 μm).

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may be relatively short (potentially resulting in incomplete bonding), or may be separated by significantly longer periods of time. The rate at which delamination occurs also may vary over several orders of magnitude, depending on whether, for example, 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 as substrates) add to the complexity of designing a controlled-release surface.

Silicone release coatings based on polydimethylsiloxane (PDMS) networks are the workhorse release materials used in the pressure sensitive label industry [1]. Their low surface energies ($18-22\,\mathrm{m \cdot Nm^{-1}}$ over a fiftyfold variation in cross-link density [2]) and chemical inertness limit the extent of wetting, the thermodynamic work of adhesion, and specific chemical interactions between the PSA and release coating, leading to fascile peel release forces. However, release forces are often lower than optimal and the relative changes with delamination rate may be undesirable for the application at hand. In these situations, a high-release additive (HRA) is commonly utilized to provide some level of release force control to the system.

Functioning as a major component in a HRA, silicate resins are incorporated into the silicone network as release modifiers although the resulting effect on the release mechanism is not clearly understood [1, 3, 4]. Controlling release force properties – and doing so in an accurate and consistent way – remains arguably the most difficult technical challenge in silicone release coating technology. The impact of a HRA on the surface properties (energy and topography) of the silicone coating and on the release mechanism has been analyzed extensively by workers at our laboratories using liquid contact angle measurements, a contact mechanical approach based on the Johnson–Kendall–Roberts (JKR) theory [5], atomic force and phase-measurement interference microscopy techniques, and profilometry. The contribution of the surface properties to the silicone/HRA release mechanism was determined to be secondary to the viscoelastic contributions and was reported elsewhere [6].

This paper, while acknowledging that some finite contribution from the surface/interfacial energetics is required for some adhesion to occur between the silicone coating and PSA, will focus on the

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energy-dissipative contributions of these viscoelastic components to release force profiles obtained over three decades of delamination rate. The primary contribution of the silicate resin-based HRA is assumed to result from its impact on the viscoelastic properties of the PDMS network. The object of this study was to characterize the viscoelastic properties of HRA-modified solventless silicone release coatings and two representative PSAs and to determine the impact of these properties on the release profiles. A general mathematical model, based on existing adhesion models, is proposed to help design release systems (release coating and PSA properties) to achieve desired release force profiles.

2. EXPERIMENTAL

2.1. Solventless Release Coatings

The thermal solventless release coatings with varying levels of HRA were prepared *via* platinum-catalyzed addition-cure chemistry [1]. Release coating 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.

2.1.1. Vinyl Functional Polydimethylsiloxane

The polymer component of the release liner was a vinyl-terminated and -pendant PDMS with an average of 30 dimethylsiloxane units between vinyl groups on the PDMS backbone. Size exclusion chromatography (SEC), using columns calibrated with PDMS standards, revealed a weight-average molecular weight M_w of $18.7\,\mathrm{kg\cdot mol^{-1}}$ with a polydispersity M_w/M_n of 2.2.

2.1.2. Release Modifier

The release modifier was based on a vinyl-functional (2 wt%) silicate resin with an average M_w of $20.6 \pm 0.5\,\mathrm{kg\cdot mol^{-1}}$ and polydispersity near 4, based on polysilicate-calibrated SEC measurements. The polymer component of the primary HRA in this study (designated as

HRA-1) consisted of a 22 mPa · s vinyl-terminated PDMS functioning as a reactive diluent. Alternatively, a secondary HRA (HRA-2) formulation consisting of the silicate resin and the base PDMS (2.1.1) was utilized to generate additional release force data and assist in determining the model-fitting parameters. The weight fraction of silicate resin in each HRA was held constant.

2.1.3. SiH Functional Cross-linker

With a platinum complex as a catalyst for the hydrosilylation reaction, a trimethylsiloxy-terminated poly(dimethylsiloxane-co-methylhydrogensiloxane) copolymer was used as a cross-linker at an excess ratio of silicon hydride to vinyl groups (SiH : Vi) of 1.4 to optimize cure.

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2.2. Organic Pressure-sensitive Adhesives

Industry standard tapes for determining the performance characteristics of silicone-coated release liners were selected to represent two major adhesive technologies: the tesa® 7475 acrylic- and 7476 rubber-based adhesives with PVC and cloth backings, respectively. A Solutia Gelva® RA – 1753 acrylic adhesive was also employed for comparative purposes.

Table I summarizes the average thickness of each tesa® tape component measured using scanning electron microscopy (JEOL JSM – 6100). Figure 1 shows a typical micrograph of the tape cross-section. In instances where adhesive was smeared across the interface during sample preparation *via* freeze fracturing, the average adhesive thickness was calculated by solvent-extracting the adhesive prior to measuring independently the thickness of the liner and the adhesive backing.

TABLE I Analysis of tesa® tape cross-section using scanning electron microscopy

	Thickness, μm	
Component	*tesa*® 7475	*tesa*® 7476
Adhesive backing	40	190
Adhesive	82	40
Release liner (silicone coating + backing)	58	60
Total	180	290

2.3. Measurements

2.3.1. Release Profiles

Peel testing to profile release force as a function of peel rate (from 5.08 to 5080 mm · s^{-1}) was conducted with the Instrumentors 3M90 Slip/Peel and ZPE – 1000 High-Rate Peel Tester. Tests were performed on 25.4-mm wide laminates aged for at least one day at room temperature by peeling the release liner from the adhesive using a 180° peel angle at ambient conditions.

2.3.2. Rheological Properties

Release coating test specimens 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, it ensured intimate contact between the test fixtures. The Rheometric Scientific RDSII and RDAII dynamic mechanical spectrometers provided a torque transducer range of 0.02 – 200 mN · m. To remain above the lower limit of the transducer sensitivity, the terminal flow regime of the adhesives at 25°C was characterized using 25-mm diameter parallel plates. To access deformation frequencies corresponding to the peel rates, isothermal, frequency-sweep experiments were performed in shear deformation within the linear viscoelastic region from 30°C to below the glass transition temperature. Because thermal solventless silicone release coatings are rapid-cure systems at relatively low temperatures, it was assumed that the bulk properties of the test specimens prepared under different cure protocols for the peel and rheological measurements were identical.

3. RESULTS

3.1. Release Force Profiles

Figure 2 shows release force profiles for silicone-coated liners – modified with various levels of HRA-1 – peeled from the tesa® adhesives at a 180° angle under ambient conditions. All the peels at different rates were relatively smooth: the root-mean-square values for

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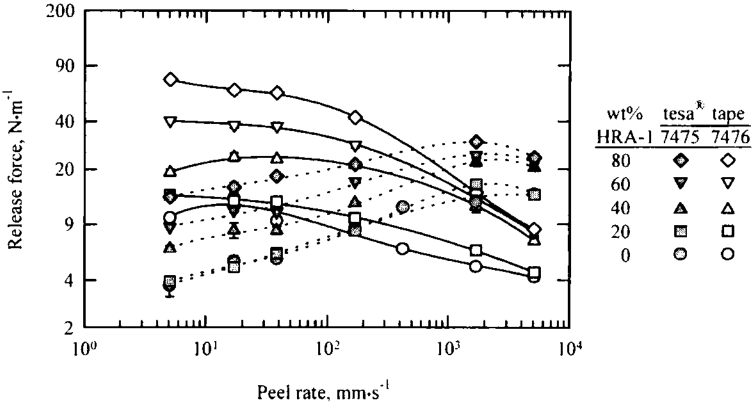

FIGURE 2 Logarithmic plot of release force as a function of peel rate for a silicone-coated liner (modified with 0–80 wt% HRA-1) peeled at a 180° angle from two different PSA tapes: the tesa® 7475 with an acrylic-based adhesive and PVC backing, and the tesa® 7476 with a rubber-based adhesive and cloth backing.

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release averaged 9 and 15% for the acrylic and rubber-based adhesives, respectively. The release forces all increased with HRA-1 content at a constant peel rate. However, contrasting release profiles were obtained between the tesa® 7475 acrylic- and 7476 rubber-based adhesives over the entire range of delamination rates. For the former, release force steadily increased at rates below 10^3 mm · s^{-1} prior to displaying a maximum value after which a slight decrease was apparent. For the latter, release force did not vary significantly at low peel rates before exhibiting a decreasing profile at peel rates above 400 mm · s^{-1}. In all cases, an increase in release coating HRA content resulted in higher release forces at any given delamination rate, with the greater impact observed at lower peel rates. Figure 3 shows that these characteristics remain qualitatively consistent when using a different release modifier (HRA-2).

3.2. Viscoelastic Properties of Release System Components

3.2.1. Viscoelastic Properties of PSA Component

High-performance PSAs, which are typically utilized in a cured state, must have the capability to form physical bonds efficiently with

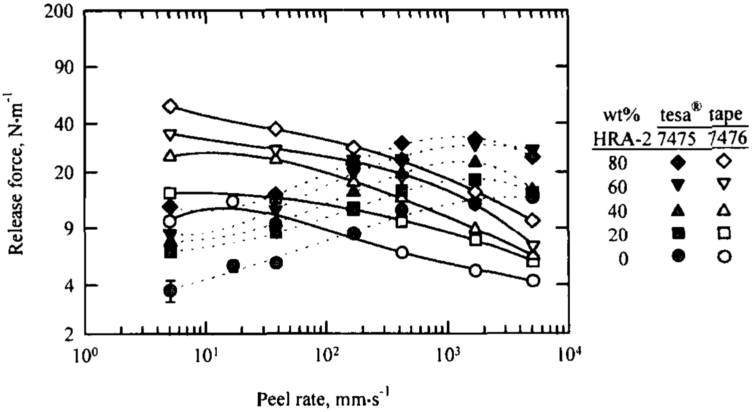

FIGURE 3 Logarithmic plot of release force as a function of peel rate for a silicone-coated liner (modified with 0–80 wt% HRA-2) peeled at a 180° angle from two different PSA tapes: the tesa® 7475 with an acrylic-based adhesive and PVC backing, and the tesa® 7476 with a rubber-based adhesive and cloth backing.

substrates under relatively low frequency conditions and to resist debonding under considerably higher frequency peel conditions. To accomplish both tasks with one material, it is reported that a low modulus is required under bonding conditions [7] and a significantly higher modulus with a large dissipative component is required under the higher rate debonding conditions [8, 9]. Consequently, PSAs typically have very dynamic moduli profiles near standard use temperatures and frequencies. Figures 4 and 5 show the shear storage (G') and loss (G'') modulus and the loss tangent ($\tan\delta = G''/G'$) master curves generated for the acrylic- and rubber-based adhesive materials (unsupported) using isothermal, frequency-sweep experiments and time–temperature superposition principles [10]. The two adhesives chosen for this study were based on industry standard tapes and represented two major adhesive technologies: the tesa® 7475 acrylic- and 7476 rubber-based adhesives.

The release force data were collected over a delamination rate range of 5–5000 mm·s^{-1} at 25°C. The effective dynamic frequency (ω) of deformation imposed on each of the system components can be related to the rate of delamination (v) by accounting for the thickness (h) of a given component in the peel test through the Eq. (1) [11]

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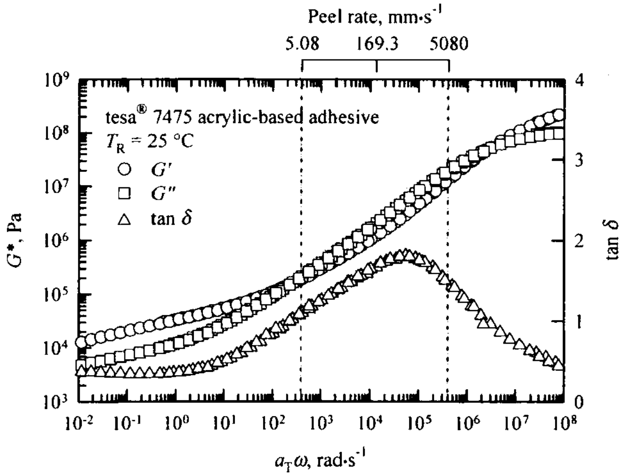

FIGURE 4 Rheological master curves for the tesa® 7475 acrylic-based pressure sensitive adhesive at a reference temperature of 25°C.

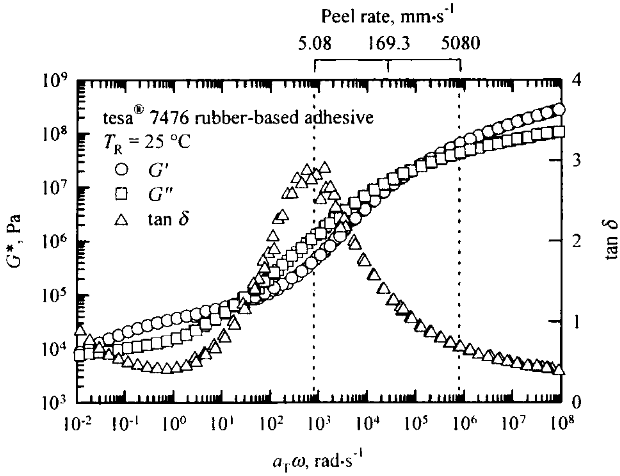

FIGURE 5 Rheological master curves for the tesa® 7476 rubber-based pressure sensitive adhesive at a reference temperature of 25°C.

$$v = \frac{\omega}{2\pi} h \tag{1}$$

Based on the measured thickness of each adhesive, the resulting frequency window which corresponds to the delamination rates used in this study for the acrylic ($h = 82\,\mu m$) and rubber ($h = 40\,\mu m$) adhesive is depicted by the dotted vertical lines in Figures 4 and 5, respectively.

3.2.2. Viscoelastic Properties of Silicone Release Coating Component

Figures 6 and 7 show the rheological master curves using a reference temperature of 25°C for a cured, silicone release coating modified with three different levels of HRA-1 and HRA-2, respectively. Within the same frequency range, the modulus profiles of the release coatings are considerably less dependent on frequency compared with the master curves for the PSAs shown in Figures 4 and 5. However, it is apparent that the addition of the release modifier enhanced the loss modulus G'' (and hence tan δ) of the release coating to a greater extent than that of the storage modulus G'. Equation (1) also describes the influence of the thickness of a viscoelastic material on the effective frequency at a given delamination rate. Therefore, because the loss modulus is a function of frequency, varying the thickness of the release coating

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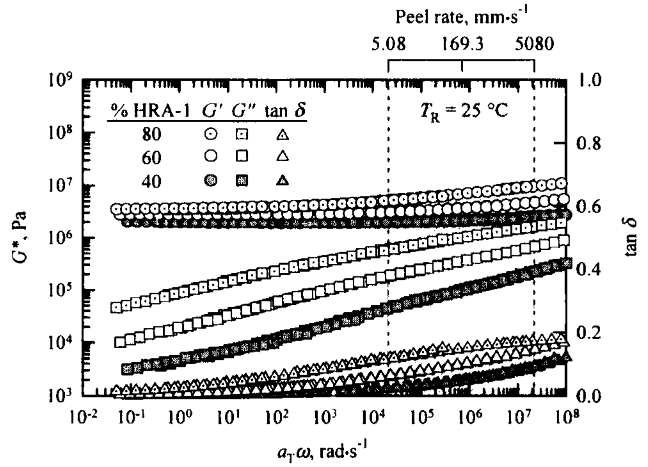

FIGURE 6 Rheological master curves at a reference temperature of 25°C for the release coating material at the three highest HRA-1 concentrations. The dotted lines bracket a three-decade frequency window determined from Eq. (1) corresponding to the range of rates used in peel testing based on a nominal coating thickness of $1.5\,\mu m$.

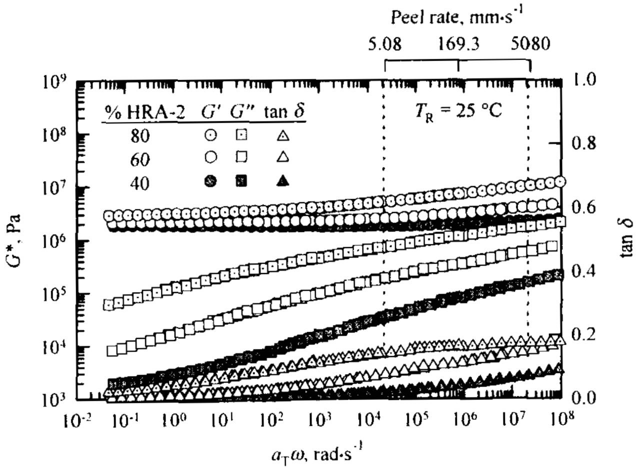

FIGURE 7 Rheological master curves at a reference temperature of 25°C for the release coating material at the three highest HRA-2 concentrations. The dotted lines bracket a three-decade frequency window determined from Eq. (1) corresponding to the range of rates used in peel testing based on a nominal coating thickness of 1.5 μm.

impacts its ability to dissipate energy at a constant delamination rate which, in turn, affects the magnitude of the release force [6].

4. DISCUSSION

Surface properties of release liners for PSAs are clearly important for enabling the development of a release system. The low surface energy of silicone release coatings, which limits the work of adhesion and molecular entanglement that can develop at the interface between the silicone coating and organic PSA, provides the basis for the widespread use of silicones as release coating materials. However, once these initial requirements for release are satisfied, the viscoelastic properties of the system components are hypothesized to play the primary role in controlling the release force required for delamination and in manipulating how the release force changes with delamination rate. Hence, the following discussion is a focused look at the viscoelastic properties of the system components and their impact on release force.

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4.1. Qualitative Comparison of Release Force Profiles with Component Viscoelastic Properties

Figures 2 and 3 reveal the release force profiles obtained when peeling a PDMS/HRA release coating system from two different PSAs. Although the release coatings are identical in each figure, contrasting release profiles for the different PSAs highlight the need to control more than just the PDMS/HRA ratio to tune the release force profiles. The tesa® 7475 acrylic-based adhesive exhibits increasing release forces with increasing peel rate, whereas the tesa® 7476 rubber-based adhesive peel rate has almost an opposite impact.

Figure 4 shows the storage (G') and loss (G'') modulus and the ratio of the latter to the former, $\tan\delta(G''/G')$, as a function of frequency for the acrylic-based PSA. As the deformation frequency increases from 10^{-2} to $10^{8}\,\mathrm{rad\cdot s^{-1}}$, a steady increase in both the storage and loss moduli is observed, but $\tan\delta$ exhibits a maximum in the glass–rubber transition regime where the loss modulus approaches, and sometimes exceeds, the storage modulus. In this transition regime, the material displays viscoelastic behavior which – as the term suggests – is intermediate between viscous flow and elastic solid behaviors. On both the low- and high-frequency sides of the viscoelastic regime, the storage modulus dominates the loss modulus as manifested by a low $\tan\delta$ function; thus, the material behavior is largely elastic.

Potential explanations for the dramatic differences in the release profile shapes may be found in the viscoelastic property profiles of the two adhesive materials (Figs. 4 and 5). In the frequency ranges corresponding to the test peel rates, the positions of the $\tan\delta$ maxima appear to approximate the relative positions (peel rates) of the release force maxima for each adhesive. With each ordinate representing one decade, Figure 8 compares release force, from an unmodified (0% HRA) silicone liner, with the dynamic loss tangent functions of the tesa® 7475 acrylic-based and tesa® 7476 rubber-based adhesives as a function of the peel rate. The loss tangent, being a function of the dynamic frequency of deformation, ω, can be related to the peel rate, v, by accounting for the adhesive thickness, h, as described by Eq. (1). For the adhesive, $\tan\delta$, which is a measure of the relative amount of energy dissipated to that stored per cycle of deformation, appears at least to be able to describe qualitatively the varied release profiles

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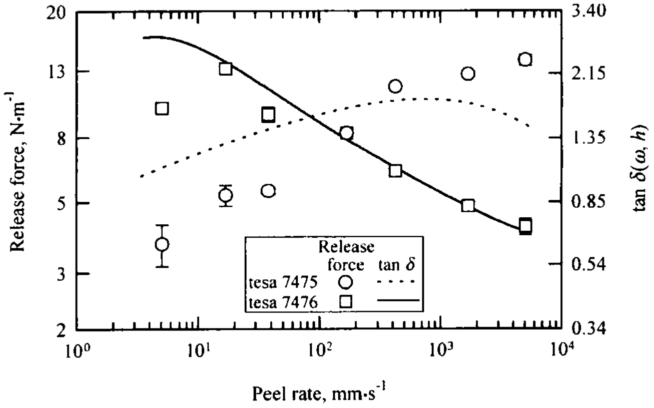

FIGURE 8 Logarithmic plot correlating release force, from an unmodified (0 wt% HRA) silicone-coated liner, and the dynamic loss tangent functions of the tesa® 7475 acrylic-based and tesa® 7476 rubber-based adhesives as a function of the peel rate.

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commonly observed in PSA/release systems. Release force data of a rubber-based adhesive tape from a release liner previously reported by Chang and Wang [12] also showed the presence of a maximum as a function of peel rate and is often observed in practice.

4.2. Adhesion Models

Relating the energy dissipative character of an adhesive to the peel force obtained is certainly not novel. In the late 1960s to early 1970s, Gent [8, 13–15]; Schultz [8]; Andrews [16]; Kinloch [14, 16] and Kaelble [17] reported that the strength of an adhesion system is partially dependent on the intrinsic strength of the interface and largely dependent on the relative ability of the adherends to dissipate energy viscoelastically under the conditions of the test. Based upon these principles, Tse [11] proposed the general expression in 1989 to describe PSA tack, T:

$$T = P_0 BD \tag{2}$$

where P_0 is the thermodynamic work of adhesion, and B and D are the bonding and debonding terms, respectively. P_0 (which can also be expressed as an intrinsic surface energy, I) is dependent only on

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bonding forces acting directly at the interface and is generally much smaller in magnitude than the debonding term (D). D was proposed to be proportional to the amount of energy dissipated by the adhesive as represented by the loss modulus at a debonding frequency (ω_d) corresponding to the tack debonding rate, $G''(\omega_d)$. On the other hand, B was described to be a constant as long as the Dahlquist criterion was satisfied: the storage modulus of the adhesive is less than 0.33 MPa at frequencies corresponding to bonding conditions, ω_b [7].

In 1991, Yang [18] proposed that bonding is a kinetic process that depends on the viscoelastic nature of the adhesive under bonding conditions. The bonding term was associated with the relative area of contact the adhesive established with the substrate and that the term was rationalized to be proportional to the creep compliance of the adhesive. The creep compliance is approximated by the inverse of the adhesive storage modulus at the relative bonding frequency, $\omega_b(B \propto [G'(\omega_b)]^{-1})$, under conditions that the adhesive is predominantly elastic ($\tan\delta \ll 1$, $G' \gg G''$) at the bonding frequency. By relating the debonding term to the dynamic loss modulus of the adhesive at the debonding frequency, $D \propto G''(\omega_d)$, Yang [18] proposed that the adhesive strength, P, of a PSA is related to its linear viscoelastic properties:

$$P \propto I \frac{G''(\omega_d)}{G'(\omega_b)} \tag{3}$$

where ω_b and ω_d are the effective bonding and debonding frequencies, respectively.

Equation (3) is very attractive because it relates peel force to readily measurable linear viscoelastic properties of the adhesive. However, its acceptance has been limited by the realization that large deformations and, hence, nonlinear behavior typically accompany the debonding of high performance PSAs. In 1985, Andrews [19] cautioned against using linear viscoelastic parameters such as $\tan\delta(\omega)$ to describe the energy dissipation in a nonlinear event such as the peeling of a high-performance PSA from a high energy substrate. Recently, Pocius and co-workers [20] proposed using a generalized Maxwell model to take into account the extensive stranding that occurs during debonding of most PSAs.

4.3. Release Model

4.3.1. Comparison of Peel and Release Systems

One of the goals of this work was to use the aforementioned adhesion models as a basis from which to model a release system based on viscoelastic property parameters. To accomplish this objective, it is important to realize the major differences between a typical peel system (a PSA bonded to a high-energy substrate such as a metal) and a release system (a PSA laminated to a low-energy release coating). Table II provides a qualitative comparison between both PSA-based systems.

Literature reports on PSAs generally address the peel testing of adhesives from high-energy substrates at low peel speeds resulting in high peel forces and a variety of failure mechanisms (adhesive, cohesive, or chaotic adhesive/cohesive failure) [21]. Release coatings, by design, exhibit low surface energy and efficient release systems fail adhesively under relatively low peel forces. As a result, the extent of deformation within the adhesive in a release system is limited, which makes the use of a release model based upon the linear viscoelastic properties of the components plausible. Because the surface energy of an organic adhesive typically exceeds that of the release coating, thermodynamic considerations suggest it is incumbent on the silicone coating to wet the surface of the adhesive during bonding. Hence, when the two materials are brought into contact it will be the molecular mobility of the PDMS network strands in the cured silicone liner, rather than the PSA, that will dictate the rate and extent of bonding. To rationalize the preceding statement, consider the following extreme cases: (1) a drop of low surface energy silicone placed on a higher surface energy adhesive film will proceed to wet the adhesive surface with the rate dependent predominantly on the surface and

TABLE II Peel system/release system comparison

Parameter	*Peel system*	*Release system*
Peel force	High	Low
Deformation	High	Low
Failure mode	Cohesive/Adhesive/Slip Stick	Adhesive
Surface energy	$\gamma_{\text{substrate}} > \gamma_{\text{adhesive}}$	$\gamma_{\text{adhesive}} > \gamma_{\text{release coating}}$
Peel rate range	Narrow/Slow	Broad/Fast

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viscous forces at the interface; (2) in contrast, a drop of an organic adhesive placed on a silicone release coating will not spread over the lower energy silicone surface.

In the manufacturing of adhesive tapes and labels, the wet PSA is often mechanically forced to spread over a cured silicone release coating supported by a paper backing, immediately followed by the curing of the adhesive. The PSA-coated release liner is next laminated with a face stock (the eventual PSA backing) to form a release system construction. The bonding of the adhesive and silicone are forced and the bonding extent is likely dependent on more than just the viscoelastic properties of the cured components.

4.3.2. Release Model Components

Considering the existing adhesion models, the differences between a peel and release system and the apparent correlation between the tan δ profile of the PSA and the release force profile discussed in Section 3.1, a general release-force model is proposed which assumes that energy is dissipated uniformly throughout the bulk of each viscoelastic component in the release system, and that release modification is a consequence of changing the bulk property of the silicone release coating component:

$$F_R(v) \propto I \times \left[\tan\delta(\omega_d, h)^{\beta_1}\Big|_{\text{PSA}} + \left(\frac{G''(\omega_d, h)}{G'(\omega_b)}\right)^{\beta_2}\Bigg|_{\substack{\text{release}\\ \text{coating}}} \right] \qquad (4)$$

where the loss tangent, tan δ, of the PSA and the loss modulus, G'', of the release coating are measured at the effective peeling frequency, ω_d. However, the storage modulus, G', of the release coating is measured at the bonding frequency, ω_b. This term is analogous to that used in Yang's model $[G'(\omega_b)_{\text{PSA}}]^{-1}$ which accounted for the kinetic aspect of the bonding process. For a release system, the time-dependent creep compliance, $J(t)$, of the release coating is used because wetting of the organic PSA by the silicone is thermodynamically favored while the reverse is unfavorable. The approximation utilized by Yang ($J(t) \sim 1/G'(\omega)$) is expected to be valid because the release coating system in this study is essentially elastic ($G' \gg G''$) regardless of the HRA concentration.

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The backings of the release coating and the adhesive are assumed to be elastic over the frequency ranges of interest and are excluded from the debonding energy dissipation components of Eq. (4). Measured viscoelastic property profiles of both the PVC and cloth adhesive backings of the PSAs used in this study confirmed their highly elastic character over the pertinent frequency range. This is not to say that the backings do not influence the observed release forces. The modulus and thickness of an elastic backing can influence the actual peel angle in the debonding regime which, in turn, impacts the stresses in the adhesive and how effectively it dissipates energy. The viscoelastic properties of most backings are assumed to have minimal impact on the release force profile because their loss modulus is essentially independent of frequency over the practical range of delamination rates.

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4.3.3. Estimation of Release Model Fitting Parameters, β_i

Initial estimates of the β_i empirical fitting parameters from Eq. (4) were attempted with the data in hand. When a solventless silicone release coating does not contain a high-release additive (HRA), the loss modulus is small compared with the storage modulus and both moduli are relatively constant over the entire applicable frequency range. Hence, the release coating $G''(\omega_d, h)/G'(\omega_b)$ term in Eq. (4) is relatively constant and can be neglected for this case, reducing Eq. (4) to

$$F_R(v) \propto I \times \tan\delta(\omega_d, h)^{\beta_1}\big|_{\text{PSA(silicone coating without HRA)}} \qquad (5)$$

The release force profiles of the acrylic and rubber PSAs from the unmodified release coating (0% HRA), and the loss tangent of these adhesives at the effective frequency of the peel delamination speeds, can be used to estimate β_1 as shown in Figure 9. Values for β_1 of 0.73 ± 0.11 and 2.44 ± 0.74 were obtained for the rubber and acrylic adhesives, respectively. The β_1 values likely depend upon a number of factors related to the PSA including the thickness of the adhesive and flexibility of the backing. The acrylic adhesive is approximately twice as thick (82 μm *vs.* 40 μm) as the rubber adhesive. Hence, more adhesive is available to dissipate energy and potentially lead to the stronger relation (larger β_1) of release force to $\tan\delta$ of the acrylic adhesive.

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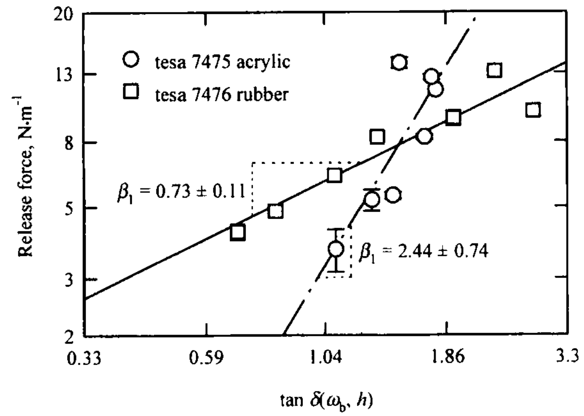

FIGURE 9 Logarithmic plot correlating release force, from an unmodified (0 wt% HRA) silicone-coated liner, and the dynamic loss tangent functions of the tesa® 7475 acrylic-based and tesa® 7476 rubber-based adhesives.

The incorporation of a HRA into the silicone network was shown to increase both the release force (Figs. 2 and 3) and the loss modulus (Figs. 6 and 7) significantly. An estimate of the β_2 parameter can be achieved by taking into account the change in release force and viscoelastic properties – due to the incorporation of HRA – by realizing that the $\tan\delta(\omega_d, h)$ of the adhesive is constant at a given delamination rate for any given adhesive. For a given delamination rate, v_x, the change in release force, ΔF_R, from the incorporion of HRA reduces Eq. (4) to

$$\Delta F_R(v = v_x) \propto \left(\frac{G''(\omega_d, h)}{G'(\omega_b)}\right)^{\beta_2}\Bigg|_{\text{release coating}} \tag{6}$$

For peel test specimens aged for at least one day, the corresponding bonding frequency is on the order of $10^{-5}\ \mathrm{s}^{-1}$. Based on their master curves (Figs. 6 and 7), the equilibrium elastic modulus for the HRA-modified release coatings can be effectively considered as $G'(\omega_b)$. However, the $G''(\omega_d, h)$ values vary significantly depending on the amount of HRA that has been added to the release coating and the debonding frequency which occurs at much shorter time scales.

Consequently, a logarithmic plot of the change in release force, ΔF_R, *versus* the viscoelastic contribution from the HRA-modified release coating, $G''(\omega_d, h)/G'(\omega_b)$, will provide an estimate for β_2 at each delamination rate for each adhesive as shown in Figures 10 and 11. Release force and rheological data of the release coating systems based on both HRA-1 and HRA-2 were utilized to provide a statistically confident estimate of β_2.

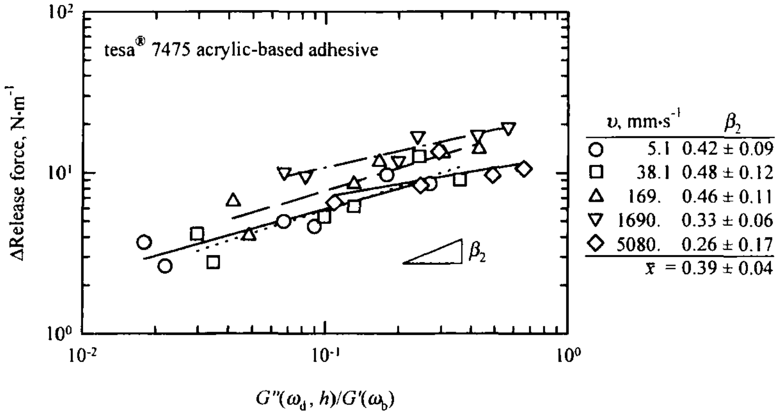

FIGURE 10 Logarithmic plot of the change in release force due to the incorporation of release modifier and a viscoelastic function of the release coating using the tesa® 7475 acrylic-based adhesive at different peel rates.

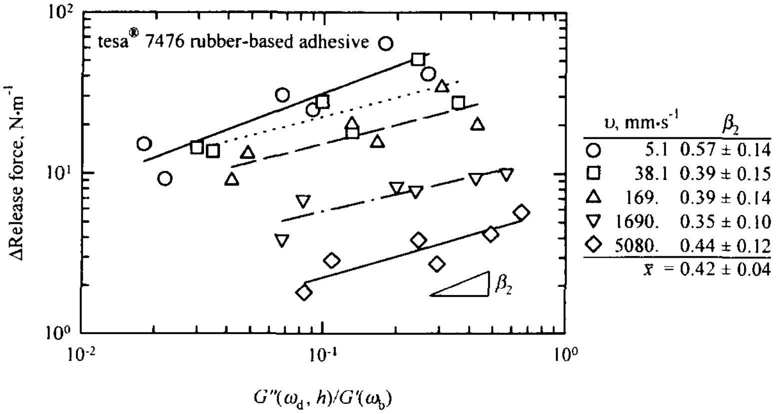

FIGURE 11 Logarithmic plot of the change in release force due to the incorporation of release modifier and a viscoelastic function of the release coating using the tesa® 7476 rubber-based adhesive at different peel rates.

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If the role of the HRA in the release mechanism is solely due to a bulk viscoelastic modification in the release coating, the scaling exponent, β_2, should be independent of the type of adhesive forming the interface with the silicone. There was insufficient evidence to reject the hypothesis that there was no difference in the mean values for β_2 ($p = 0.52$) obtained from each adhesive. Therefore, the average contribution of the HRA to the release mechanism for the release coating system used in this work may be represented using a β_2 value of 0.41 ± 0.03, which reduces Eq. (4) to

$$F_R(v) \propto I \times \left[\tan\delta(\omega_d,h)^{\beta_1}\Big|_{\mathrm{PSA}} + \left(\frac{G''(\omega_d,h)}{G'(\omega_b)}\right)^{0.41(\pm 0.03)}\Bigg|_{\substack{\text{release}\\ \text{coating}}} \right] \qquad (7)$$

where I and β_1 are dependent on the nature of the organic adhesive. The β_i parameters describe the extent to which the linear viscoelastic properties of the release system components contribute to the debonding process. Factors that could influence this contribution may include the interfacial properties (surface energy, roughness, and the distinctness of the interface), the thickness of each component, the stiffness of the backing, and the peel angle. Within the scope of this study, the exponent β_2 parameterized the viscoelastic (energy-dissipative) contribution from essentially one type of release coating system because both the silicate resin – used in the high-release additives – and the silicone network were not varied.

4.3.4. Application of Release Model

The results presented here suggest that the organic adhesive dictates the release profile because of its large energy-dissipating capability relative to the other components in the release system. This hypothesis was tested by using a Solutia Gelva® RA-1753 acrylic adhesive, which was characterized and found to exhibit viscoelastic properties similar to the tesa® 7475 adhesive (Fig. 12). The RA-1753 adhesive was laminated either onto a Mylar™ or stainless steel backing to a nominal thickness of 24 μm, less than one-third the thickness of the acrylic adhesive in the tesa® 7475 PSA construction. As delineated in

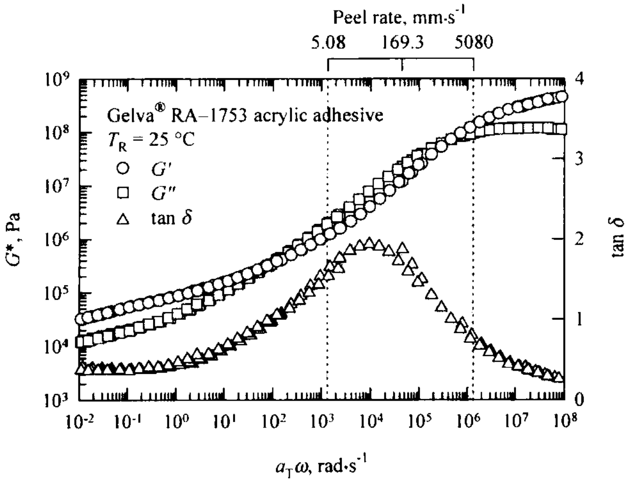

FIGURE 12 Rheological master curves for the Gelva® RA-1753 acrylic-based adhesive at a reference temperature of 25°C. The frequency window corresponds to a thickness of 24 μm.

Figure 12, the effect of decreasing the adhesive thickness is to shift to higher frequencies the window shown in Figure 4 corresponding to the range of delamination rates used in peel testing in accordance with Eq. (1). Hence, the tan δ profile of the RA-1753 adhesive suggests that the release force maximum will occur at much lower delamination rates than will occur with the thicker tesa® 7475 adhesive. Figure 13 shows that the resulting release profiles for silicone liners with two different HRA-1 loadings could be satisfactorily explained in terms of the loss tangent profile of the RA-1753 acrylic adhesive. Comparison of Figure 13 with the tesa® 7475 release profile in Figure 2 confirms a release force maximum at lower delamination rates for the release system based on the RA-1753 acrylic adhesive. The results in Figure 13 also showed that neither of the elastic adhesive substrates contributed substantially to the energy dissipation process and, hence, to the release force profiles obtained. Hence, it is apparent that release profiles can be altered and tuned significantly by simply varying the adhesive thickness with prior knowledge of the linear viscoelastic properties. A high-release additive can then be added to the silicone coating to manipulate further the magnitude of the release forces while maintaining the same profile trends.

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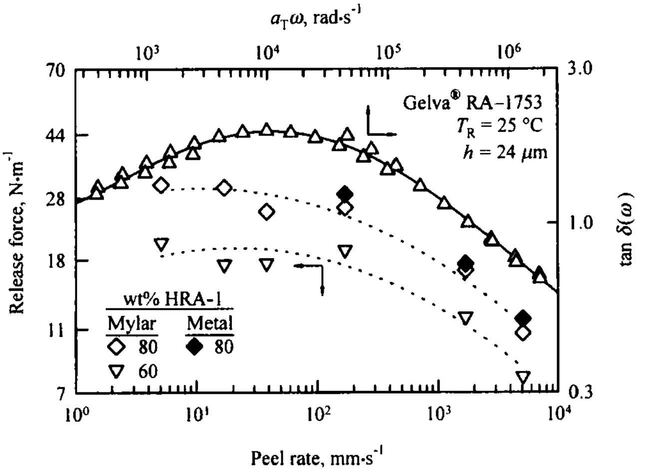

FIGURE 13 The release profiles for a silicone-coated liner containing different levels of HRA-1 and peeled at an 180° angle at ambient conditions. The release-force data were obtained from a Gelva® RA-1753 acrylic adhesive coated to a nominal thickness of 24 μm on either a 51-μm-thick Mylar^{TM} or a 1-mm-thick stainless steel substrate, and compared with the dynamic loss tangent function of the adhesive in the frequency range corresponding to the delamination rates used in the peel tests.

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5. CONCLUSIONS

Surface properties of release liners for PSAs are clearly important for enabling the development and application of a release system. The low surface energy of silicone release coatings, which limits the work of adhesion and molecular entanglement that can develop at the interface between a silicone coating and organic PSA, provides the basis for the widespread use of silicones as release coating materials. However, once these initial requirements for release are satisfied, the viscoelastic properties of the system components are shown to play a primary role in controlling the release force and manipulating how the release force changes with delamination rate.

In this work, the release force of an acrylic- and rubber-based PSA from solventless silicone release coatings containing different levels of HRAs were measured as a function of peel rate. The release profiles differed dramatically for the two different adhesive types. The general trends of either increasing or decreasing release force profiles with peel rate are proposed to be predominantly due to the relative ability of the adhesive to dissipate and store energy ($\tan\delta$) over the operating frequency range. The addition of a high-release additive to the release coating enhances dissipative character (G'' and $\tan\delta$ increased) of the silicone network and, hence, the release forces obtained. However, in the systems studied here, it appears that adhesive type and thickness must be chosen properly along with an appropriate HRA concentration to achieve the desired release force level and profile.

Inspired by existing adhesion models, an empirical model based on the viscoelastic properties of the adhesive and release coating was proposed to describe release force profiles. The viscoelastic properties of the release coating are assumed to contribute to both the extent of bonding and the total energy dissipated during debonding. This complicates the model development when compared with existing models for the adhesion of PSAs to high-energy substrates. However, the low peel forces in release systems, which enable adhesive failure over broad delamination rates and limit PSA deformation during debonding, allow more confidence in the use of linear viscoelastic properties to describe release force behaviors.

Utilizing the release force and viscoelastic property data for the materials used in the study, the β_i fitting parameters of the model were estimated. The release model was also shown to predict successfully the potentially significant impact of adhesive thickness on the release force profile using an acrylic PSA which was not employed in the model development. The use of vastly different elastic backings with the acrylic PSA was shown to have negligible impact on the shape of the release force profiles. This observation provided initial confirmation that ignoring the properties of elastic backing materials in the release model is potentially valid.

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