Release Force Understanding – Recent Findings

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Abstract

The practical application of elastomeric polydimethylsiloxane coatings for the release of organic adhesives has been advanced at an accelerated rate by applying fracture mechanic principles to what was previously viewed as a complicated surface energy problem. Through the efforts of several research groups, including the work spearheaded by M. Chaudhury, new insights have been gained about the role release plays in applications ranging from bio-fouling to organic pressure-sensitive adhesives. The rapid increase in learning can be attributed to the reduction of diverse release problems to a single, unifying approach and by considering the frictional and viscoelastic forces operating across the siloxane-organic interface.

Introduction

For many years, the primary considerations in the development of pressure-sensitive adhesives (PSAs) were the ultimate substrate (including paper, metal, the human body and organic plastics) and operating temperature. Typically, little or no consideration was given to the nature of the elastomeric polydimethylsiloxane (PDMS), or silicone, release coating that was in contact with the PSA for storage and pre-positioning purposes. However, two recent trends have brought about a change in focus: 1) the globalization of the paper, label and tape industries, and 2) increasing regulatory pressures to convert to environmentally friendly products.

The globalization of the PSA industry has led to a greater emphasis on economy of scale. This has resulted in reduced or simplified product offerings and a greater emphasis on the production process. High-speed production methods employing low-temperature-cure solventless coatings applied to the cheapest substrates available have placed practical constraints on silicone release coating designers. As a consequence, studies on wetting/adhesion, substrate poisoning, film splitting and network formation have received intense consideration. While the palette of available polymers has been shrinking, expectations for release force levels and degree of release force separation have not. In fact, the release coating is being asked to compensate for the economic-based modifications of the organic PSA; e.g., the incorporation of extending monomers (which add little to PSA viscoelastic properties) or the reduction in PSA thickness/coat weight. To meet the growing demands of the PSA industry, a greater understanding of the molecular basis of release is necessary so network and process demands can be better matched with optimum conditions for controlled release.

The greatest technological challenge is applying a 1-micron-thick silicone coating homogeneously over a macroporous substrate composed of acrylic resin, mineral particulates and cellulosic fibers. The degree of cure and homogeneity of coverage are the two most studied attributes. This is because deficiencies in either can have catastrophic consequences. Cheaper substrates generally have a less well-defined surface structure and a greater incidence of substances that poison the release coating’s precious metal catalyst. These substrates can also negatively impact anchorage to the backing. High-speed coating processes (with their shorter residence times in costly gas-fired ovens, short wet-out times and...
atomization of the coating solution during roll splitting) impose viscosity—and therefore viscoelastic—limitations. Environmental constraints have dictated the use of solventless systems, which has created additive solubility issues and reduced the effective molecular weight of polymers and crosslinkers.

The PDMS elastomeric network is typically treated as if it were a single, unambiguous entity. However, no single polymer system offers the degree of freedom afforded by silicone chemistry. Figure 1 illustrates the silicone chemistries utilized in the majority of the industrial and academic studies. There is a great deal of controversy surrounding adhesion hysteresis and the relative role of bulk versus interfacial effects. This lies in the lack of a clear understanding of the subtleties of the roles Si–H and Si–Vi play in the architecture of the starting materials, which include silicone hydride crosslinkers and vinyl-functional polymers, high-release additives (HRAs) based on methyl silicate resins and a precocious metal catalyst. In silicone release applications, there are unprecendented architectural options available, from the mundane degree-of-polymerization to the more complex degree-of-branching. These freedoms can be combined with reactivity changes between vinyl- or hexenyl-functional polymers, likewise between –OH(–CH₂O)₅–, –CHₓSiH, and –O₂SiH. This, coupled with their low glass transition temperature (Tₓ)*, is why PDMS-based polymers are often used to study crosslinkers. The same degree of freedom is also observed in HRAs based on methyl silicate resins. All major silicone release coating manufacturers have commercial versions of the methyl silicate resin. While these versions perform the same function, they may vary significantly in composition, molecular weight, degree of reactive functionality and, hence, in ease of dispersion, reactivity and efficacy in modifying release.

The conventional explanation for the efficiency of PDMS as a release coating is its low surface energy; PDMS release coatings have solid surface tensions in the region of 18 to 22 mN m⁻². However, low surface energy, by itself, does not guarantee excellent release performance; other factors, such as interfacial dynamics and viscoelastic considerations, also play important roles. Early studies by Chaudhury and Whitesides [1] of the adhesion between monolayer fluorocarbon- and hydrocarbon films supported by elastomeric PDMS established that the adhesion hysteresis for the fluorocarbon monolayer was significantly higher than for the hydrocarbon monolayer. Chaudhury [2] further observed that when adhesives were peeled from PDMS surfaces, a sliding or lateral displacement, as tracked by fluorescent markers [3], could be observed several hundred microns from the crack tip. It was also revealed that, depending on the release surface, peel velocity and peel geometry, the magnitude of this induced sliding could account for 50 percent of the overall peel fracture energy.

In Chaudhury’s sliding experiment, a semispherical PDMS slider layer was slid over mica-supported fluorocarbon and hydrocarbon self-assembled monolayers yielding friction and adhesion hysteresis data on both systems. The adhesion energies for compressive and decompressive loads with the fluorocarbon monolayer were 32.2 and 62.7 ergs cm⁻², respectively, whereas the alkyl surface yielded equivalent values of 38.4 and 45.6 ergs cm⁻², respectively. In the former case, the hysteresis (D = 30.5 ergs cm⁻²) was significantly higher. The normalized friction force (interfacial shear strength) for the PDMS fluorocarbon monolayer was 21.4 dyn cm⁻², which was significantly higher than the value of 4.6 dyn cm⁻² obtained for the PDMS/hydrocarbon monolayer. The friction force values did not follow the trend of surface-free energies: the fluorocarbon surface had a value of 9.5 ergs cm⁻² compared to the hydrocarbon surface value of 19.3 ergs cm⁻². This was clearly in contradiction to Dupre’s thermodynamic consideration of adhesion.

One polymer property that follows this trend, as well as the similar trend illustrated in Figure 2, is Tₓ. Wynne and co-workers [4] have proposed that such molecularly flexible substrates prevent adhesive mechanisms, such as mechanical interlocking on rough surfaces, from operating. Professor Chaudhury’s work on the influence of surface states on adhesion hysteresis and frictional properties has spurred work by others in these fields [5-8]. It was observed that in elastomeric PDMS systems, low-release surfaces also possessed the lowest friction [5,9]. Both adhesion and friction are determined by polymer chains close to the surface; the segmental mobility of these polymers is altered by their proximity to an interface. When a PDMS elastomer is placed in contact with either a similar or dissimilar surface, reconstruction of surface polymer chains will occur. The nature and extent of this reconstruction will determine the level of adhesion and its ultimate stability. The adhesion hysteresis of extracted and non-extracted PDMS substrates residing against the same and dissimilar substrates has been studied by many researchers [10-12]. In some studies, adhesion hysteresis due to induced hydrogen bonding was encountered; while in others, Pt catalyst complexation, or Pt catalyst-induced hydrosilylation across an interface, was reported as a root cause. In industrial release applications, Pt-catalyzed release coatings containing high residual levels of silicon hydride groups react with the carboxyl groups on some acrylic-based adhesives, leading to increasing peel forces and, ultimately, to acrylic “lock up.” The release force observed in a freshly constructed laminate is typically lower than the release force observed in the same laminate after it has aged for several days. It is presumed that the non-equilibrium conditions encountered during the construction process lead to surface restructuring and a resulting increase in molecular contact. Calculations by Israelachvili [5] lead one to conclude that the interdigitation is not part of the surface restructuring between the two immiscible layers because we do not see a continuous increase in release forces after time. The reconstruction at the interface, which leads to the initial increase in release, is due to conformational changes in the organic polymers with higher Tₓ. Pressure-sensitive adhesives—including those that incorporate a soft rubber segment—are still less molecularly mobile than the low-Tₓ PDMS coating.

Chaudhury’s work sought to quantify the energy directly related to the interfacial process and separate it from the bulk deformation process. We have sought to extend that knowledge to the fabrication and performance of industrial PSA laminates. With the help and guidance of Chaudhury and his research group, we have begun to deconstruct the interfacial and bulk contributions to the control of release force at higher peel velocities [13].

Experimental

Solventless silicone coating systems containing modulating levels of HRA were prepared via addition-cure chemistry. All vinyl-functional polymers were stripped on a wipe film evaporator to 95.5 percent or greater non-volatile content, as measured by 3-hour weight-loss measurements at 150°C. The mixing ratios for all systems involved 100 parts...
vinyl-functional PDMS (with or without HRA), 0.7 parts of a maleate inhibitor and 2 parts of Sys-OFF® 4000 Platinum Catalyst. The crosslinker used throughout these studies was Sys-OFF® 7678 Crosslinker, a dimethyl-methylhydrogen-siloxane copolymer with an SiH content of 1.1 wt %.

The 1.5-µm-thick test specimens were cured onto 54.5-µb Niccol paper at 205°C for 6 seconds. For viscoelastic measurements, 1.3- to 1.6-mm-thick samples were crosslinked in situ at 130°C for more than 3 hours, enabling real-time monitoring of the extent of cure and, more importantly, ensuring complete contact between the 8-mm-diameter parallel plate fixtures of the rheometer. Samples for lateral-force microscopy, interfacial slippage, and indentation were prepared in accordance with published methodologies. Industry standard PSA tapes were selected to control the release profile, while the organic adhesive, can be tuned through the choice of the silicone release surface and its viscoelastic characteristics.

Other practical considerations, such as the effect of adhesive thickness on release force, could also be accounted for in the debonding process. The work, which combined forced-displacement measurements with visual observations, was able to delineate the energetics of the various processes involved in separation/release of glass and metal probes from organic adhesives. In Figure 4a, an initial dewetting process was followed by the formation of singularities at the interface, which in turn became the site of fibrils formation. The bulk of the dissipation process being observed involved the stretching of the fibrils.

In Figure 2, time-temperature superposition was used to characterize the viscoelastic response of two adhesive families (solvent-based acrylic and styrene-butadiene rubber) within the time scale of the peel test. The shaded data symbols in Figure 2 represent the experimental peel velocities used in generating the 180-degree peel data. It was evident from the general shape of the resulting release profiles that the inclining or declining profile observed in release force versus peel speed had its origins in the bulk viscoelastic properties of the PSA. Later in this paper, we will show how control of the release profile, while dominated by the organic adhesive, can be tuned through the choice of the silicone release surface and its viscoelastic characteristics.

Recent works by Shull [15, 16] have used nano-indentation with hemispherical and flat punch probes to advance the understanding of the molecular basis for the viscoelastic process observed in the debonding process. The work, which between crosslinks. As the dp between crosslinks increased, the release force in the high-speed domain increased. Conversely, release force decreased in the low-speed domain. The net result of these two opposing trends is a general increase in the release profile with increasing dp.

Figure 6 plots the bulk viscoelastic properties of these networks, and others with even higher dp, between crosslinks.

Equation 1. \( \omega = \frac{2\pi v}{h} \)

This made it possible to match viscoelastic events with the application time constant over the four decades observed in practical peel testing [14]. In Figure 2, the profiles have been normalized for thickness, using the data from the thinnest adhesive (\(h = 0.015\) mm) as a reference. Because the data did not collapse into a single curve, it was apparent that other factors influence the observed release force (\(F_R\)). Figure 3c shows that by applying a vertical shift factor (b), there is a reasonable superposition of data in the intermediate and high peel speeds. If adhesive failure energy (\(G_F\)) is assumed to be independent of adhesive thickness at a particular peel velocity (v), this would suggest that the actual peel angle (θ) decreases as \(h\) increases. Hence, from the relationship illustrated in Equation 2, an increase in release force values should be expected.

Equation 2. \( G_F = (1 - \cos \theta) F_R \)

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Bistac [7] used pin-and-wheel tribometry measurement together with peel testing to study adhesion and friction of PDMS against glass. In polymer-only networks, a more pronounced increase in peel force was found in networks with greater distances between crosslinks, a trend that increased with increasing separation rates. Higher dp leads to a greater quantity of free and pendant chains linked by one end only. Bistac argued that this increase in surface mobility creates better surface wetting and increased contact point, hence higher adhesion strength on separation. The separation energy was greatest at higher speeds because, at high speeds, the viscous resistance to chain slippage becomes more important. It was also observed that the higher-dp polymers had lower friction, yet higher adhesion. This finding was attributed to the formation of a highly mobile surface layer, a consequence of free ends with poor cohesion and shear resistance. Bistac’s measurements were made at low peel speeds just bordering on those typically used in practical PSA applications shown in Figure 2.

Chaudhury [18], working across a much broader velocity range (10^{-1}–10^3 m·s^{-1}), also found that friction decreased with increasing molecular weight, while increasing as a function of velocity. A peak in shear stress as a function of velocity, and independent of molecular weight, was observed. The peak at 10^3 m·s^{-1} coincided with the inversion zone of the peel results shown in Figure 5. While it is dangerous to make comparisons between two very different separation methodologies, it would appear that there is a broad transition from slippage-controlled release in the low-speed domain to dissipative properties associated with higher-molecular-weight polymers. It is unclear whether this is describing the transition from interfacial to bulk rheological control. Considering the sample configuration and peel angle, it is possible (as previously suggested) that the high-speed results in this system are a result of a coupling of the bulk viscoelastic properties of the release coating and the adhesive.

In practical applications, the viscosity limitation engendered by multi-roll, high-speed coaters and the decrease in cure speed with increasing dp results in mainly PDMS polymers with dp in the entanglement limit being used in solventless release coatings. Without the ability to broadly tailor molecular weight, the level of adhesion best suited for a given PSA application is achieved through the addition of an HRA to the silicone release coating. Figure 7 shows the combined effect of changing the dp of the vinyl-endblocked polymer and the HRA loading levels measured using an SBR tape aged for 28 days. Peel force versus peel speed reveals a trend toward an increase in low-speed peel force and a reduction in high-speed peel force as HRA levels are increased. The net effect is a reduction in the maximum peel force at intermediate peel speeds with almost flat profiles at the highest HRA loading level. Practical coat weight limitations prevent the study of higher loadings of HRAs. Amouroux’s system differed significantly from that of HRA levels tested. In this study, the methyl silicate HRA. The methyl silicate structure used in this study contained no self-section dimethylsiloxane units, and reactive vinyl functionality was present only as vinylidimethyl silyl groups. Such gross changes in architecture make direct comparisons difficult. An example of this would be the reduction in slippage that Amouroux reported when going from 20 to 40 wt % HRA, whereas Figure 9 shows no slippage at any of the HRA levels tested. In this

![Figure 6. Effect of crosslink density of PDMS networks from vinyl-terminated precursors on the loss modulus (G'*) at a frequency of 10 rad·s^{-1} and a reference temperature of 25°C.](image)

![Figure 7. Release force versus peel speed as a function of polymer dp and HRA loading level.](image)

![Figure 8. Lateral-force microscopy data for PDMS with 0 to 34 wt % methyl silicate high-release additive.](image)

![Figure 9. Interfacial slippage data for PDMS with 0 to 34 wt % methyl silicate high-release additive.](image)

![Figure 10. Shear stress as a function of sliding velocity for a PDMS coating with 0 to 24 wt % methyl silicate high-release additive.](image)
paper, we advocate surface pinning of the adhesive due to a universal reduction in surface mobility rather than direct, HRA-only, pinning of the adhesive as postulated by Amouroux. In previous work [20], no evidence was found for systematic changes in surface tension, nano-roughness or chemical composition in our systems that would explain the systematic change many groups have observed. The data presented is consistent with Brown’s [21] observations that increasing the rigidity, i.e., reducing the flexibility, of the surface increases friction. This freezing of the surface results in an increase in the threshold stress supported at the interface and practical release force level.

Conclusion

Low peel speed results showed a decrease in peel (release) force as a function of increasing polymer molecular weight. At intermediate peel speeds of 10⁻¹ m·s⁻¹, this dependence changed from decreasing to increasing force with increasing molecular weight. It is proposed that the molecular conformation of the silicone network at the separating interface controls the transition in the fracture process from one in which surface slippage circumvents the dissipation of force (resulting in easy release) to a more rigid surface capable of sustaining higher stress levels.

Chaudhury had proposed a release mechanism for cured PDMS-based release coatings in which interfacial slippage minimizes the bulk shear deformation experienced by the organic adhesive. The data presented here are consistent with this mechanism. Commercially used silicone release coatings exhibit interfacial slippage. Traditional HRAs used in release coatings “freeze out” interfacial slippage, resulting in increased adhesive deformation. The HRA reduces the segmental mobility of the PDMS chains within the cured network leading to increased shear stress and an increase in practical peel force. It is proposed that the mobility of the surface states, as controlled by the dp between crosslinks and the HRA content, simply allows for more efficient use of the viscoelastic dissipation states of the adhesive.

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