Influence of Surface Interactions on Pressure Sensitive Adhesive (PSA) Performance

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Introduction

Pressure sensitive adhesive (PSA) performance is related to a combination of rheology and surface science. Even in the early days of PSA development, criteria that related performance to moduli, such as the Dahlquist criterion (Dahlquist, 1959), were identified. On the other hand, the relationship between surface energetics and performance has been a more muddled path, partly because it is so difficult to separate surface energetics from rheology. Most efforts to directly measure the surface interactions of PSAs also result in some mechanical distortion. This paper summarizes several approaches that may provide some insight and can serve as a basis for future, more thorough studies.

Classical Theory of Adhesion

Most textbooks start with the premise that the work of adhesion can be related to surface energies of the substrates and adhesives. If a material fails adhesively, then at least from a thermodynamic point of view, the interface between the adhesive and substrate is being altered to a case where each interface is in contact with air rather than one another. The work associated with the separation should be entirely related to surface energy if it is assumed that there are no deformations during the process (Figure 1).

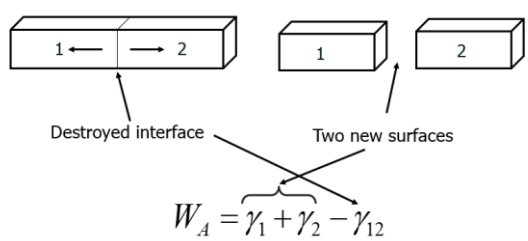


Figure 1. Classical Work of Adhesion Experiment

where

W_A = the work of adhesion per unit area
γ_1, γ_2 = Surface energy
γ_{12} = Interfacial energy

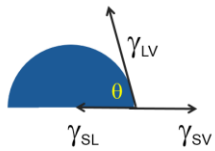
A typical surface energy for polymers would be around 35 dynes/cm (same as ergs/cm^2). If the interfacial tension is assumed to be small, then the peel force for peeling adhesive from a polymer substrate should be 2γ. Since γ for a typical acrylic PSA is around 35 dynes/cm, that gives us:

2.54 cm/in x 2 (sides) x 35 dynes/cm x 10^{-5} Newton/dyne = 0.0018 Newton/in of peel force

The discrepancy between this value and the actual measured peel forces, which are typically several Newtons for acrylic PSAs, is mainly attributed to rheological effects. Taking this analysis at face value, it may seem like surface energetics do not contribute to the peel force. However, if there were no interactions whatsoever, then the adhesive would release from the substrate before rheological effects could come into play. Stronger surface interaction will permit greater rheological forces to be withstood

before the adhesive releases from the substrate. In other words, a relatively weak force at an interface can be markedly amplified through rheological deformation processes.

A common myth in PSA technology is that the adhesive must wet the substrate and higher surface energy adhesives have poor wetting of lower surface energy substrates. At first glance, there is a temptation to compare the wetting of PSA on a substrate to how a liquid wets a substrate. For liquid wetting and contact angles, most simply consider a three-phase system of the substrate, the liquid, and air. In this case, it is well known that higher surface energy liquids can de-wet and form beads on lower surface energy substrates. A prime example is water on silicone release liners. Young's equation states:



$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$$

Figure 2. Young's Equation for Liquid Drop on Substrate

Where γ_{sv}, γ_{sl}, and γ_{lv} is the surface tension between the solid/vapor phase, solid/liquid and liquid/vapor phase, respectively. γ_{sv} is often referred to as the surface energy of a solid. γ_{lv} is often referred to as the surface tension of a liquid. γ_{sv} is often referred to as the interfacial surface tension.

In many cases (but not all), the interfacial surface tension is small. If it is <u>assumed</u> that interfacial tension is zero, then the criteria for a liquid spreading on a solid ($\theta = 0$) is when the liquid surface tension (γ_{lv}) is less than or equal to the solid surface energy γ_{sv}.

In terms of a free energy analysis, spreading will be spontaneous when the change in Gibb's free energy is less than zero:

$$\Delta G = \gamma_{LV} + \gamma_{SL} - \gamma_{SV}$$

If a drop of liquid is applied to a surface, all surfaces and interfaces are described in Young's equation. As a structure becomes more complex, such as a PSA label or tape applied to a substrate, more interfaces and boundary conditions must be considered to completely understand thermodynamic equilibria.

Substrate Wetting

When a waterborne liquid is coated onto a solid substrate, the value of γ_{sv} can have a profound effect on wetting:

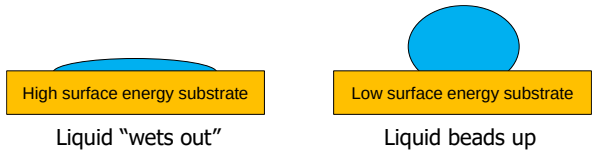


Figure 3. Wetting a Surface in the Presence of Air

However, in the case of PSA bonding the system above is oversimplified because it assumes air is the top layer. PSAs bond two surfaces together, so there is virtually always another surface besides air involved in any construction (that is, the face stock). One can easily see the consequence of altering the system in this manner by placing a second sheet of release liner atop the water drops. Immediately they will spread and make a more or less continuous film (Figure 4). When a few drops of water are placed on the liner, the vast majority of the liner consists of a silicone air interface and to a first approximation, the total free energy is given by the surface energy just of the release liner. Since the water occupies such a small area, say 5%, its contribution will be on the order of 5% x 72 dynes/cm or ~4 dynes/cm.

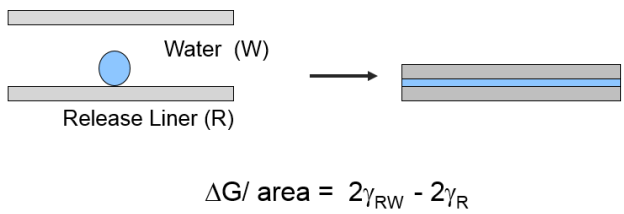
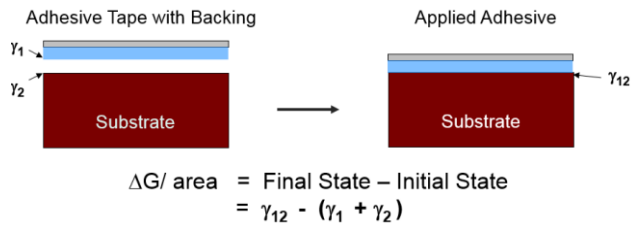


Figure 4. Water between Two Layers of Release Liner

The interfacial tension between silicone oil and pure water is 35 dynes/cm (F. Peters, 2013) and surface energy for silicone liner is around 19 dynes/cm. The ΔG is 16 dyne/cm (or ergs/cm^2). Based on this value, the water should not spread. However, the water also has to support the weight of the facestock which requires an additional 5 dynes erg/cm^2 force. This primitive estimation suggests that there should be a weak receding force of about 11 dynes/cm^2. A small amount of additional pressure can easily overcome this small resistance. Moreover, even low levels of impurities can significantly depress the surface tension of water and also act to lower interfacial tensions. Finally, if the surface tension of the water droplet that was neglected in the calculation is considered, that should also decrease this value.

The water drop on a silicone liner is among the most extreme cases of sandwiching a material between two others. For acrylic PSAs, the most extreme practical case is applying the adhesive to a low energy surface such as polyolefins. Acrylics PSAs are mostly polymerized with C4 esters or greater and have surface energies in the low to mid 30s dyne/cm. Polyolefin surfaces generally have a surface energy somewhat lower than acrylics and are typically in the low 30s dyne/cm. Interfacial tensions between the two surfaces are generally cited on the order of 5 dynes/cm (Brandrup, 1989). In the case of applying a label or tape to a surface where the PSA is ultimately sandwiched between the two, the initial state can be considered to have two planer surfaces exposed to air.



$\Delta G = 5-(30+35)$ dynes/cm = - 60 dynes/cm.

Figure 5. Free Energy Change of Adhesive Being Applied to a Substrate

By surface energy standards, -60 dyne/cm is a strong spreading force and hence there is no need for additional wetting agents for acrylics to wet polyolefin surfaces. They will wet the surface as long as they can overcome any rheological resistance.

Since acrylic PSA labels and tapes wet virtually all surfaces in end-use applications from a thermodynamic point of view, the problem now reduces to this: how do compositional changes affect the strength of surface interactions? In the work of adhesion equations, the main issue with determining changes in free energy is that the interfacial tension, γ_{12}, cannot be readily measured. In absence of such data, estimations of γ_{12} can be made from the polar and dispersive components of surface tension. When the contact angles are measured for various known liquids on a surface, analyzing the data set not only results in the determination of the solid's surface energy (γ), but also its polar (γ^p) and non-polar/dispersive (γ^d) components.

$$\gamma = \gamma^d + \gamma^p$$

In his work, Wu (Wu, 1971) reported that a good approximation for interfacial tension was:

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d\gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p\gamma_2^p}{\gamma_1^p + \gamma_2^p}$$

Since the polar and dispersive components for many common polymers are tabulated in the literature, works of adhesion can be easily calculated for several systems. Table 1. Work of Adhesion Based on Wu's Equationlists surface energies taken from Accudyne (Accudye, Inc, 2017) and works of adhesion using the interfacial tension from the Wu equation. For a given polymer system, the work of adhesion (or cohesion if the substrate is identical to the adhesive polymer) is calculated from three common substrates: aluminum, polyethylene, and silicone. Note that the surface energy of clean aluminum should be quite high; however this substrate is very easily contaminated during processing and storage. These results indicate that the very low polarity of silicone PSAs should lead to lower adhesion. What may be somewhat surprising is how many cases the analysis at this level does not even predict trends of what is commonly observed with pressure sensitive adhesives. For example, the trend in the work of adhesion results is that if higher adhesion is required, a more polar adhesive should be used.

Table 1. Work of Adhesion Based on Wu's Equation

	Surface Energy (ergs/cm^2)			Work of Adhesion on Substrate: (ergs/cm^2)		
	γ	γ^d	γ^p	Al	HDPE	Silicone
Aluminum foil	41.2	31.7	9.5	82.4	69.4	52.4
Poly 2-ethylhexyl acrylate	30.1	28.9	1.3	65.0	64.1	48.7
Polyethylene (PE)	34.2	32.8	1.4	69.4	68.4	51.1
Polyethylene terephthalate (PET)	43.7	36.6	7.2	84.3	73.9	54.8
Polyisobutylene (PIB, butyl (rubber)	33.6	33.6	0	65.2	66.4	48.9
Polymethyl acrylate (PMA)	41.4	35.6	5.8	81.5	72.8	54.1
Polymethyl methacrylate (PMMA)	43.5	35.9	7.8	84.5	73.3	54.5
Polypropylene (PP)	30.1	27.7	2.4	66.8	63.6	48.7
Polystyrene (PS)	41.7	37	5	81.4	73.9	54.7
Polyvinyl acetate (PVA)	37.7	24.8	13	77.6	61.5	48.0
Poly n-butyl acrylate	32.2	28.6	3.6	70.6	65.1	49.8
Polydimethylsiloxane (PDMS)	20.5	19.2	1.3	52.4	51.1	41.0

One hypothesis often cited is that adhesives made with 2-ethylhexyl acrylate (EHA) have better adhesion on HDPE than those made with butyl acrylate (BA) because it is closer to the surface energy of HDPE. This level of analysis predicts the contrary. Nevertheless, actual interfacial tension measurements have been reported for the pairs BA/PE (5.0 ergs/cm^2) and EHA/PE (3.1 ergs/cm^2) (J. Brandrup, 1989). Using these values, the work of adhesion for both BA/PE and EHA/PE are 61.2 ergs/cm^2.

There are very few homo-polymer PSAs. Most acrylic emulsions have at least some polymerized acid or other hydrophilic or polar comonomers. In addition, emulsions contain many other species that are surface active and might give much different surface characteristics than that described by literature values for homo-polymers. One might argue that the failure of homo-polymer surface energies to correlate to actual works of adhesion may be due to these other monomers in the composition. To test the merit of this hypothesis, a series of polymers with different amounts of acid and polar comonomers were synthesized and surface energies were measured by standard techniques. One might speculate that low molecular weight surface active species might interact with test fluids used to determine surface energy. To avoid any artifacts from such effects, adhesives coated on 2 mil PET were rinsed with copious amounts of water to remove any surfactant at the surface. SIMS spectra of the rinsed surfaces confirmed that virtually all surfactant had been removed and the surfaces consisted of polymeric material. Contact angles were measured and the polar and dispersive components were calculated. The following acrylic PSAs were tested:

Sample ID	Polar Comonomer (wt%)	Acid Comonomer (wt%)
Adhesive A	0	0.8
Adhesive B	0.5	0.8
Adhesive C	0.5	1.0
Adhesive D	0	1.25
Adhesive E	0	1.5
Adhesive F	0	2.3

Table 2. Measured Surface Energies and Work of Adhesion to HDPE

Sample	Adhesive A	Adhesive B	Adhesive C	Adhesive D	Adhesive E	Adhesive F
Total	25	25.4	26.1	31.5	25.6	26.2
Polar	4	4.9	2.9	7.4	2.2	2.7
Dispersive	21	20.5	23.2	24.1	23.3	23.5
δ_{12} (HDPE)	1.6	1.8	0.9	0.6	0.8	0.8
Work	53.4	53.6	55.2	60.9	54.8	55.4

The surface energies measured in this series are significantly lower than what is reported for typical acrylic polymers. If anything, the addition of acid, or polar comonomer should increase the surface energy over the reported values of EHA or BA. On the other hand, many of the values fall within a very narrow range of 25 to 26.2 dynes/cm so the difference here may be due to the specific liquids and reference values used in the calculation. The lower surface energy of less polar monomers should preferentially orient at the surface (air interface) and perhaps this is why there is relatively little impact from the addition of low level, more polar components. If this is the case, then one might expect that surface energies would fall in a 2 dyne/cm^2 range as does EHA and BA homo-polymer.

Even with the limited success within the present series, it difficult to see what insight the data provides. Since the above adhesives have significant differences in rheology, there were no efforts made to relate the data to performance. Coupling this with the data on homopolymers, there is no clear evidence that surface energy has much of an impact, at least when looking at acid level. Moreover, others in academia have concluded that surface energy has only a secondary effect on adhesion (Abbott, 2015).

At first pass, it seems that the work of adhesion which is at the core of adhesion theory, appears to explain so little. Arguably, the reason that surface energy is at the core, is that these effects are always present and might be applied to any construction. What is lacking in this surface energy analysis is that many surface energy analyses do not capture all of the compositional effects and mechanisms that can arise at a surface. Adhesion can be influenced by other phenomena and in fact may be entirely dominated by factors other than surface energy. In addition to the polar and dispersive forces, adhesion may be affected by:

- Hydrogen bonding
- Covalent bonding

- Electrostatic charge
- Physical entanglements
- Diffusion/mixing across the interface

In a more rigorous evaluation, the overall work of adhesion may be represented by the sum of all these interactions.

$$W_{total} = W_{dispersion} + W_{polar} + W_{H\ bond} + W_{acid\text{-}base} + W_{covalent} + W_{electrostatic} + W_{entangle} + W_{mix}$$

Table 3. Elements Comprising the Total Work of Adhesion

$W_{dispersion}$	Van Der Waal forces present in all systems
W_{polar}	Dipoles and induced dipoles, e.g, acids, esters, alcohols, amines, amides, nitriles
$W_{H\ bond}$	Acid, Alcohols
$W_{acid\text{-}base}$	Acid/Amine, Lewis acid/base pairs
$W_{covalent}$	Aziridine, isocyanate, carbodiimide, DAAM/ADH, Oxazoline
$W_{electrostatic}$	Static charge
$W_{entangle}$	Adhesive flows around paper fibers à Paper tear
W_{mix}	Mixing at the interface to for a single phase system, e.g. Heat sealing some polyolefins

With such varied mechanisms, there can be more than one approach to vary the surface adhesion.

Chain Interdiffusion

Solubility

One pattern that is often observed in adhesives is that like likes like. This is also used as a general rule for predicting solubilities. If the chemistry of the adhesive and substrate are close to one another, an increase in adhesion is often observed. For example, silicone adhesives have better adhesion to silicone release liners than their rubber or acrylic cousins. Although the compatibility of a BA-based acrylic and PMMA (plexiglass) is not ideal, there may be some limited intermixing of functional groups very close to the surface which might create a “fuzzy” interface. Unfortunately, there are no readily available analytical methods to test the sharpness of the surface interface.

A simple model to scout interactions is the comparison of Hildebrand solubility parameters. Although there are much more rigorous approaches to solubility, the Hildebrand model can provide some basic insights by assuming that values that are closer together tend to be more soluble in one another. For example, BA and MMA are very close to one another and BA is closer to PVC than isoprene. Solubility parameters for some commonly encountered polymers are listed in Table 4.

Table 4. Hildebrand Solubility Parameters of Common Polymers

Compound	δ_h (MPa$^{1/2}$)
Poly(acrylonitrile) (AN)	26.2
Poly(ethylene terephthalate) (PET)	21.2
Poly(methyl acrylate) (MA)	20.0
Poly(vinyl acetate) (VAc)	19.6
Poly(vinyl chloride) (PVC)	19.6
Poly(ethyl acrylate) (EA)	19.1
Poly(methyl methacrylate) (MMA)	19.0
Poly(n-butyl acrylate) (n-BA)	18.9
Poly(α-methylstyrene)	18.4
Polystyrene (PS)	18.3
Poly(isobutyl acrylate) (i-BA)	18.2
Poly(isobutyl methacrylate) (i-BMA)	18.0
Poly(sec-butyl methacrylate) (s-BMA)	18.0
Poly(t-butyl methacrylate) (t-BMA)	17.6
Poly(2-hexyl acrylate) (2-EHA)	17.7
Poly(ethylene) (PE, LDPE, HDPE)	16.7
Polyisoprene (PI)	16.5
Poly(propylene) (PP)	16.2
Poly(isobutylene) (PIB)	15.8

Tackifiers

Tackifier Chemistry and Surface Enrichment

In the case of tackification of the bulk adhesive, most formulations use tackifier in the 10% to 40% range. Two common tackifier types are C5/C9 hydrocarbons and rosin esters. Rosin esters can contain a larger distribution of similarly structured material, but most list the structure shown in **Error! Reference source not found.** as a typical structure. However, during the manufacturing process, the rosin portion undergoes a disproportionation reaction so the conjugated double bonds become a 50/50 mixture of single double bonds and aromatic rings (dihydroabietic acid and dehydroabietic acid).

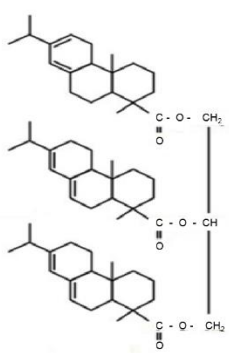


Figure 6. Base Structure of Glycerol Rosin Ester Tackifiers

In the past, it has been speculated that tackifiers are surface active and will have some enrichment at the surface even though they appear completely miscible with acrylic polymer. If there is significant surface enrichment, XPS should be able to measure it as an increase in carbon level. In order to test this hypothesis, an unformulated acrylic PSA (Adhesive C), was prepared at two different levels of tackifier. Since surfactant has the potential to confound results (surfactant may also enrich at the surface), all samples were soaked in water prior to testing. The water soak should significantly reduce surfactant

content. Adhesive C is prepared with anionic surfactants and since no sulfate is detected in the results shown in Table 5, much, if not virtually all, of the surfactant has been removed by the rinse step. In addition, the theoretical distribution of elements was calculated based on the assumption that the tackifier was distributed uniformly throughout the adhesive. This was computed by using the neat Adhesives C data and the depicted structure of the tackifier to calculate its C/O content.

Table 5. Surface Elemental Composition by XPS

		C	**O**	**Si**
Adhesive C	Average	79.5	20	0.4
	StdDev	0.6	0.5	0.1
Adhesive C + 15% C5/C9 hydrocarbon	Average	82.2	17.4	0.4
	StdDev	1.1	1	0.1
	Theoretical	*82.9*	*17.0*	
Adhesive C + 30% C5/C9 hydrocarbon	Average	86.5	13.0	0.5
	StdDev	2.1	1.9	0.2
	Theoretical	*85.5*	*14.0*	
Adhesive C + 15% rosin ester	Average	83.2	16.5	0.3
	StdDev	2.3	2.1	0.2
	Theoretical	*83.0*	*18.4*	
Adhesive C + 30% rosin ester	Average	85.5	14.4	0.1
	StdDev	1	1	0.1
	Theoretical	*83.2*	*16.7*	

For the hydrocarbon tackifier, there is no evidence of surface enrichment whatsoever. The theoretical values are well within one standard deviation. Even though there is more carbon reported at the surface for the case with the rosin ester tackifier, its enrichment is barely more than two standard deviations for the theoretical bulk value. Thus, there is no evidence that either of these tackifiers enrich at the surface. The thermodynamics seem to be entirely driven by the entropy of mixing.

It is well known that tackifiers are added to acrylic polymers to improve their adhesion to olefinic substrates. Part of how a tackifier works is related to its ability to interact with olefinic substrates, at least in the case of acrylics. In order to maintain good capability and rapid mixing in acrylics, tackifiers are designed as lower molecular weight materials (typically, <5000 amu) with high T_gs. These two attributes result in a major alteration of the rheology of the adhesive when adding tackifiers. For some polymers, such as SIS, this is the major reason for adding tackifiers. For neat acrylic polymers, rheology is much more controllable, so they are primarily added to improve surface interactions with olefinic materials. Since addition of tackifiers alters both surface interactions and rheology, a fundamental understanding which isolates the impact of each effect is more complex.

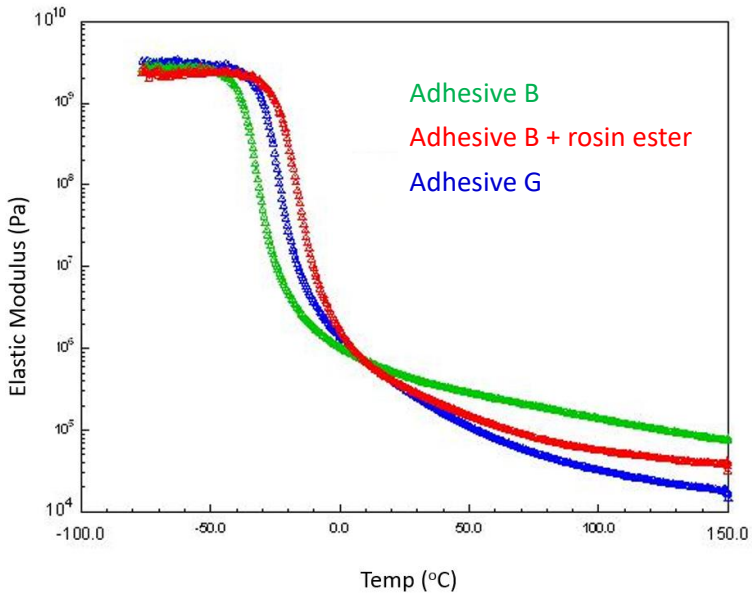


Figure 7. Elastic Moduli of Model Adhesives

If the failure mode is adhesive, lower modulus adhesives tend to have higher peel values on HDPE. In an effort to compensate for rheology changes upon tackifier addition, Adhesive G, which is an exceptionally low modulus untackified acrylic adhesive (Figure 7), was taken as the basis for comparisons. Direct coating adhesive G and adhesive B with and without rosin ester tackifier onto 2 mil PET film at 21 g/m^2 and drying at 80°C for 5 minutes resulted in the PSA data in Table 6 and confirms why tackifiers are added in acrylics. The stainless steel peel and tack data for Adhesive G (untackified) are nearly identical to the tackified Adhesive B, yet the tackified sample has superior adhesion to HDPE. Moreover, Adhesive G has lower shear than the tackified sample. In most cases, lower shear adhesives are expected to have higher HDPE adhesion. The presence of tackifier overrides this expectation.

Table 6. PSA Performance, Tackifier Addition, and Rheology Alterations

	180° Peel, HDPE (N/in, 20 min dwell)	**180° Peel, SS (N/in, 20 min dwell)**	**Loop Tack (N, HDPE)**	**Loop Tack (N, SS)**	**Shear (hr, SS, 1”x1”x1 kg)**
Adhesive G	2.8 (A)	10.5 (A)	5.9 (A)	10.6 (A)	3.2 (C)
Adhesive B	1.5 (A)	5.6 (A)	5.5 (A)	8.4 (A)	>51
Adhesive B + rosin ester	5.0 (A)	11.1 (A)	7.3 (A)	11.2 (A)	24.1 (C)

The fact that many tackifiers used in acrylics also have some limited solubility in polyolefins suggests that mechanisms other than simple surface enrichment might come into play. Unfortunately, there are no facile experiments that can probe these interfaces.

Weak Boundary Layers

Water

Surface interactions can also play a role in moisture exposure. As moisture enters an adhesive, it can enter the bulk of the adhesive where it either plasticizes the polymer or forms domains between particles. In these cases, there is typically a decrease in shear. Alternatively, the water can form a weak boundary layer between the adhesive and a substrate. In this latter case, peel should be reduced.

To illustrate the impact of water on pressure sensitive adhesive properties, each of the samples was direct coated at a 0.8 mil thickness onto PET film and laminated to panels for standard peel tests. Peel measurements were made after 24 hr dwell. One set of panels was equilibrated in a constant temperature/humidity room maintained at standard PSTC test conditions. Another set was submerged in water, which was held at 23° C, for the 24 hours. Peels were measured for this latter set immediately after removal from water along with those not exposed to water. Results are listed in Table 7.

Table 7. Impact of Water and Surfactant on Peel

180° Peel (g/in)		**Adhesive H**		**Adhesive A**		**Adhesive I**	
		As-Is	+1% DOSS	As-Is	+1% DOSS	As-Is	+1% DOSS
Stainless Steel	Dry	860 (A)	1111 (A)	581 (A)	585 (A)	738 (A)	785 (A)
	H_2O Soak	544 (A)	373 (A)	24 (A)	63 (A)	293 (A)	142 (A)
	Retention	63%	34%	4%	11%	40%	18%
HDPE	Dry	543 (A)	429 (A)	400 (A)	416 (A)	453 (A)	283 (A)
	H_2O Soak	507 (A)	0 (A)	113 (A)	0 (A)	366 (A)	0 (A)
	Retention	93%	0%	28%	0%	81%	0%

In every case, the “As Is” sample maintains more of its peel on HDPE than SS. However, when excess surfactant is post added, 1% dioctyl sulfosuccinate (DOSS), HDPE for all samples drop to zero. One hypothesis is that there is competition at the surface for which species yields the lowest free energy. In more surfactant-starved systems, water is less likely to spread across the HDPE surface than the adhesive. When a sample is submerged in water, water is more apt to enrich at the more polar surface thereby creating a weak boundary layer that reduces peel. If excess surfactant is present in a system, the excess surfactant may be more apt to collect along the hydrophobic surface of HDPE which then could create a path for a water/surfactant mixture to spread along the surface of the HDPE panel.

An alternate hypothesis is that the loss in peel is related to the bulk absorption of the water; however, when studied in more detail, the results are not consistent with this theory. To test this, water uptake was measured by soaking tape direct-coated with 2 mils of pressure sensitive adhesives in water for 24 hrs and measuring the mass difference before and after soaking in water (Table 8).

Table 8. Water Uptake and Surfactant Level

	Adhesive H	**Adhesive A**	**Adhesive I**
As Is	8.9%	28%	14%

+ 1% DOSS	13.8%	30%	19%

Although Adhesive A is identified as the most water sensitive in both tests, it does maintain some HDPE wet adhesion in spite of the level of water uptake in the As Is (28%). However, Adhesives H and I with DOSS post added remains at much lower levels of water uptake yet has no measurable wet adhesion at all.

There is no evidence of water significantly plasticizing these adhesives. If the water were compatible with the polymer, one would expect a decrease in the glass transition temperatures. If it is assumed that the glass transition (T_g) of water is -136° C (Velikov, 2001) (recall T_gs are much lower than melting points) and if it is assumed that the mixture obeys the Fox equation, then even 2% water should reduce the T_g of the adhesive by ~4° C. When the T_g was measured on the films before and after exposure to water, the glass transition temperatures of all samples, as measured by differential scanning calorimetry, were found to be reduced by less than 3°C in all cases. This difference is very close to the uncertainty of the DSC calculation and suggests that the vast majority of the water should be in a separate domain than the adhesive. For the samples soaked in water, a crystalline melt transition near 0° C was detected in addition to the T_g and clearly indicates water as a separate phase. Moreover, extreme care was taken to ensure that water did not volatilize throughout the DSC analysis. Since samples H, A, and I were predominately synthesized from butyl acrylate and/or 2-ethylhexyl acrylate, monomers which have very limited water solubility, it should not be surprising that the polymers show virtually no compatibility with water. This may not be the case with more hydrophilic compositions such as vinyl acetate (VAc) based polymers.

Because the above evidence points to water entering the adhesive as separate domains, it should not be surprising that all three adhesives whiten when exposed to water. To quantify the effect, 1 mil of adhesive was coated onto PET and open films were directly submerged in water. The opacity of each sample was measured immediately after removal from water and the differences between these values and an unexposed sample are presented in Table 9. What may be somewhat surprising is that some of the samples show a slight decrease in water whitening when surfactant is post added. This is repeatable and a consequence of how the surfactant affects the domain size as the water enters the adhesive.

Table 9. Water Whitening Resistance and Surfactants

	Adhesive H			**Adhesive A**			**Adhesive I**		
	1 hr	4 hr	24 hr	1 hr	4 hr	24 hr	1 hr	4 hr	24 hr
As Is	14%	21%	28%	23%	30%	29%	0.0%	1.2%	6.9%
+ 1% Surfactant	12%	21%	28%	20%	28%	30%	0.0%	1.9%	13%

Based on this data, peel results are consistent with surface interaction effects whereas water uptake and water whitening are not.

Plasticizers

Whenever a PSA contains a high level of plasticizers, these small molecules can also form weak boundary layers. Perhaps the most noted cases are when a PSA is coated onto a plasticized vinyl face stock. As this construction is aged on liner, peels can decrease markedly over time. In Figure 8, 180° degree stainless steel peels are measured for several different adhesives on face stocks containing both

monomeric and polymeric plasticizers. All failure modes are purely adhesive. Aging was performed on release liner by placing the vinyl laminates in a 70º C oven for 3 days and then equilibrating them in the controlled temperature and humidity room (CTR) overnight before conducting peel tests. It has been shown that about 20% plasticizer enters the adhesive under these conditions. Only results from one representative sample are shown for brevity, because all adhesive/facestock combinations showed the same trend.

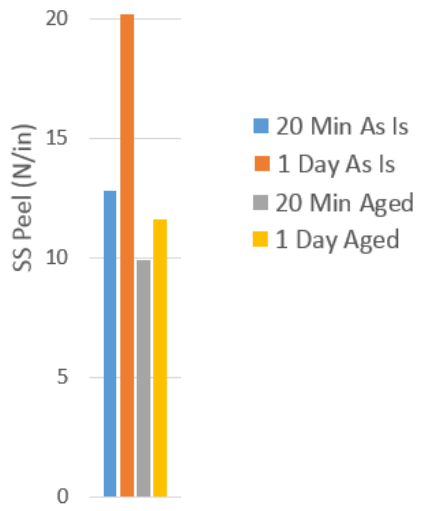


Figure 8. Effect of Plasticizer on Stainless Steel Peel

Note that the time in the key is the dwell time for the peel test. In every case, the 20 min peel "Aged" sample was lower peel than that of the 20 min "As Is" sample. In every case, the 24 hr dwell "Aged" sample was lower peel than the 24 dwell hr "As Is" sample. As plasticizer enters the adhesive, the modulus decreases and the cohesive strength decreases. One might expect peels to increase under these conditions based on rheological arguments. This implies that something is migrating to the interface that causes a loss of adhesion.

Note that even though initial peel can be greatly reduced, all of the aged samples that should be heavily plasticized do peel build to varying extents between 20 min and 24 hour dwell times. One hypothesis is that there is some compositional change at the surface. On release liner, there is little attraction between the acrylic and the liner so plasticizer may enrich at this interface. On a stainless steel substrate, the acrylic may be attracted to the metal surface more than any functionality of the plasticizer and peel build will occur.

Plasticizers can be used to enhance the performance of PSAs, in the areas of removability (US Patent No. 6586510, 2003), or to improve cold flow/wettability of crosslinked polymers (US Patent No. 9018303, 2015).

Although both tackifiers and plasticizers are small molecules that are compatible with acrylics, their response surfaces are markedly different, owing to the nature of the boundary layer that is formed.

Conclusion

Surface chemistry has a substantial effect on pressure sensitive adhesive performance. We have shown herein that measured surface energies do not completely explain differences in measured adhesion for

acrylic PSAs. Tackifiers can potentially enable us to access performance regimes not readily accessible with simple acrylic PSAs. However, tackifiers were shown to work via more complex mechanisms rather than simple surface enrichment. The effect of water was shown to be mainly due to weak boundary layer formation and absorption by interstitial domains; very little if any plasticization of the polymers by water was observed. Likewise, plasticizers can also decrease peel, although the mechanism may not be the same as water, and may be largely dependent on the polymer composition.

References

Abbott, S. (2015). *Adhesion Science.* Lancaster, PE: DEStech Publishing.

Accudyne, Inc. (2017, July 28). *ACCU DYNE TEST™ Tables of Polymer Surface Characteristics*. Retrieved from : https://www.accudynetest.com/polymer_tables.html

Brandrup, J. I. (1989). *Polymer Handbook (3rd edition).* New York, NY: John Wiley & Sons, Inc.

Brown Ian, L. N. (2003). *US Patent No. 6586510.*

Dahlquist, C. (1959). An Investiation into the Nature of Tack. *Adhes. Age Vol 2*, 25.

Kho, Dong Han, C., Hyun Ju, C., Suk Ky, K., Jang Soon, B., & Jung, Y. (2015). *US Patent No. 9018303.*

Wu, S. (1971). Calculation of Inerfacial Tension in Polymer Systems. *J. Polymer Sci.: Part C Vol 34*, 19-30.

Velikov, V., Borick, S., Angell, C. (2001). The Glass Transition of Water, Based on Hyperquenching Experiments. *Science*, Dec. 2001, 2335-2338.

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