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NOVEL APPROACHES TO THE TACKIFICATION OF PRESSURE SENSITIVE ADHESIVES

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Introduction

Pressure sensitive adhesives (PSAs) can be based on many different chemistries, such as acrylic, natural rubber latex and SIS block polymers, to name just a few examples. Regardless of the base chemistry used, adhesive performance is often optimized through the addition of various additives. In fact, a wide range of performance can be achieved by simply varying the level of certain additives. Perhaps the most commonly practiced approach has been blending tackifier into high molecular weight polymers. Over the years, many studies have interpreted these responses in terms of shifts in the glass transition temperature and modulus¹ and often assumed that the objectives were the same regardless of polymer chemistry. Such models are often cited as a means of optimizing performance.

In recent years, there has been increasing pressure on the raw materials that are commonly used to produce tackifiers. For example, as chemical manufactures are switching from naphtha to natural gas as a feedstock, there are less of the basic building blocks available that are used in the manufacture of certain hydrocarbon tackifier resins. On the rosin side, there have been appreciable fluctuations in the price of Chinese gum rosin. Some materials that were once considered as readily available building blocks now have to be more carefully optimized to achieve the most favorable cost-performance balance for use in pressure sensitive adhesives.

In some cases, a number of chemistries can be used in the synthesis of tackifiers that are compatible with a given polymer. Consequently, if there is a shortage in one chemistry users are likely to switch to another, and this often places price and demand pressures on most resins. Long term sourcing is a potential issue and even in recent years, certain grades have been close to allocation. Hence, as the most cost-effective formulations are developed for a given application the judicious use of tackifiers must be a prime consideration.

Strategies to optimize tackifier levels can be enhanced through understanding the mechanisms of how they interact with a base polymer to increase adhesion. Most approaches model adhesion in terms of rheology and surface phenomena, and a tackifier can impact both of these. Moduli as a function of temperature and frequency can readily be measured by commercially available equipment. However, surface interactions are more complex, since in any measurement, it is difficult to design an experiment that clearly separates surface effects from bulk rheological ones. Nevertheless, these effects can be inferred through careful design of experiments.

Optimization of Adhesive Rheological Modification

A tackifier can be described as a high Glass Transition Temperature (T_g), low molecular weight material. Generally, their molecular weights are under 5000 amus with T_gs that may range from around 0° C to well above 100° C. On the other hand, base polymers for adhesives typically have T_gs well below -20° C and weight average molecular weights well over 50,000 amus. Previous studies have summarized the impact that blending the two components can have. If the tackifier is compatible in the polymer, the T_g of the blend is increased and the modulus in the rubbery plateau region is decreased.

To illustrate these effects, some model systems were designed where an acrylic emulsion is formulated with tackifiers at various levels (reported as percent solids on solids) and test results are summarized in Table 1. Samples were direct-coated onto 1.2 mil BOPP at a 0.8 mil coating thickness and tested according to PSTC test methods.

Table 1. Response of an Acrylic PSA to Tackifier

	Neat Acrylic	20% Tackifier	40% Tackifier
SS Peel - 20 min dwell (N/in)	6.0 A	7.7 A	11.1 A
LDPE Peel, 20 min dwell (N/in)	4.5 A	5.3 A	8.4 A
Loop Tack, SS (N/in)	6.3 A	11.9 A	19.4 A
SS Shear, 1"x1"x1kg (hrs)	84 C	37 C	23 C
T _g (°C) by DSC	-45	-36	-23

A = Adhesive Failure, C= Cohesive Failure

In addition, thick films of these same adhesives were dried and the rheological properties were measured as a function of temperature at 5% strain and 1 radian/sec. The shear elastic modulus from the beginning of the glass transition temperature to well into the rubbery plateau region is shown in Figure 1. The increase in T_g and corresponding decrease in modulus with increasing tackifier level are readily apparent.

Figure 1. The Effects of Tackifier Addition on Elastic Modulus

In tan delta (loss tangent) plots, as shown in Figure 2, the peaks associated with the glass transition and a gradual increase in the rubbery plateau region represent the typical rheological response to tackifier addition.

Figure 2.
Effect
of
Tackifier
on
the
Loss
Tangent

It is readily evident that the tackifier is compatible with the polymer, since these responses follow the classical pattern.

One criterion that must be met to achieve high peel numbers is that the adhesive must wet the substrate. Having a lower modulus or longer dwell times will improve wetting, and tackifier addition promotes this. On the other hand, peel forces are measured by de-bonding the adhesive from a substrate. During the de-bonding process, the adhesive experiences a range of shear rates where the extension becomes quite high even during a standard 12in/min peel. Consequently, the decreased room temperature modulus and increased T_g caused by tackifier addition result in increased peel over the range studied for this particular acrylic polymer. In other instances, adding too much tackifier can cause the T_g to be too high and the resultant peel failure can become slip-stick and even decrease. Some of the negative effects of adding too much tackifier can be mitigated by using a lower softening point tackifier.

On the other hand, holding power (cohesive strength) tests occur over longer times and much slower rates. Often shear is correlated to rheology properties somewhat above the testing temperature. Since the modulus clearly decreases in the higher temperature region, a corresponding decrease in shear is noted with increasing tackifier level. Hence, even in a simple analysis such as this, one can discern compatibility issues, appropriate temperature ranges where the formulation should perform well, and rheological factors that are driving the performance.

Modification of Rheology of an Acrylic Polymer

One advantage of water-based acrylics is that a wide range of rheological properties can be engineered into the polymer, independent of the viscosity of the emulsion itself. By varying the hardness of the monomers, T_gs of the copolymers can readily be varied from below – 50 °C to well above 100 °C. Also, through careful optimization of cross-linkers, initiators, and chain transfer agents, the modulus in the rubbery plateau region can be modified to virtually any targeted value. A good polymer scientist should be able to target a glass transition temperature for an adhesive by varying composition and rubbery plateau values by varying synthesis parameters. In other words, the base polymer in the example cited above can be modified so that its rheology curve approaches one where tackifier is added to it.

As an example, consider an acrylic polymer that is designed to be tackified and a lower modulus, higher T_g analog.

Table 2. Comparison of Tackifier Addition and Neat Polymer Variations

	High Modulus Acrylic	Tackified High Modulus Acrylic	Low Modulus Acrylic (No Tackifier)
SS Peel - 20 min dwell, (N/in)	5.6 A	11.1 A	10.5 A
HDPE Peel, 20 min dwell (N/in)	1.5 A	5.0 A	2.8 A
Loop Tack, SS (N/in)	8.4 A	8.4 A	10.6 A
SS Shear, 1"x1"x1kg (hrs)	>50	24 C	3.2 C

In Figure 3, G' (elastic modulus) is plotted as a function of temperature.

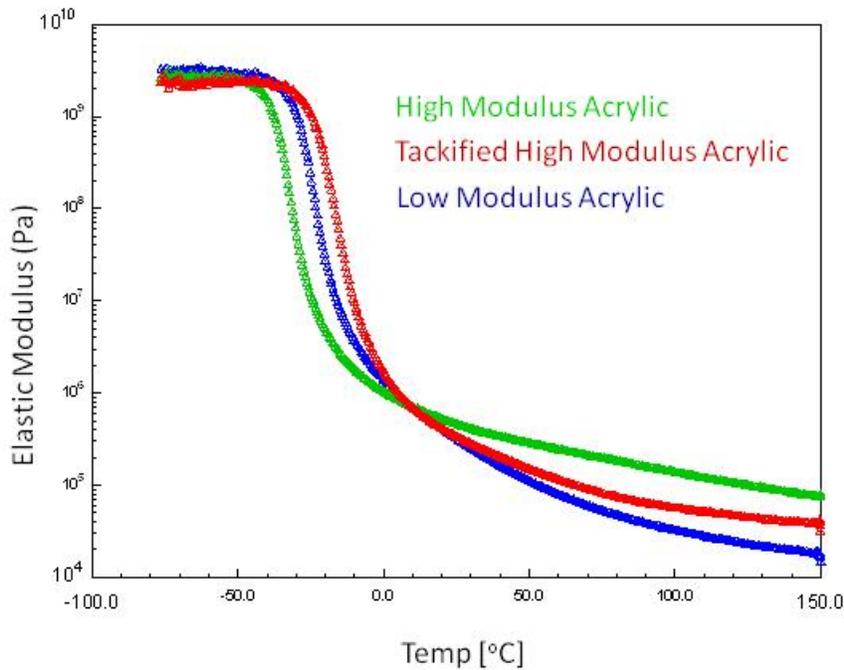


Figure 3. Comparison of Tackified and Neat Acrylic Adhesives.

One might argue that the modulus has been decreased too much for the neat acrylic to match the shear of the tackified acrylic. Clearly the only attribute that is lacking in the performance is adhesion to HDPE, a low energy substrate. However, even through experimental designs that varied synthesis parameters and glass transition could not match the HDPE adhesion of the tackified sample.

To maximize adhesion, the adhesive must be in intimate contact with the substrate. Thermodynamically, this requires that the surface energy of the adhesive must be less than or equal to the substrate to guarantee adequate spreading.

Table 3. Surface Energies of Adhesive and Substrates

	Surface Energy (dynes/cm)
Typical Acrylates used in PSA's	34-36
HDPE	31
Stainless Steel	>100

Acrylic adhesives should have no issues “wetting” stainless steel substrates from a surface energy perspective. Therefore, simply modifying the rheology of the adhesive is an effective approach if adhesion to low surface energies is not required. However, neat acrylic adhesives could have potential problems “wetting” HDPE substrates.

Surface Energy Modifications

Addition of tackifiers can also modify the surface energy of adhesives, especially for those formulated with a more polar base polymer. For example, consider the structure of rosin acid. Part of the molecule is very hydrophilic and functions to compatibilize the tackifier with more polar compositions such as acrylics. The other moiety can be thought of as being hydrophobic and has the potential to spread more effectively on hydrophobic surfaces and act much as a surfactant.

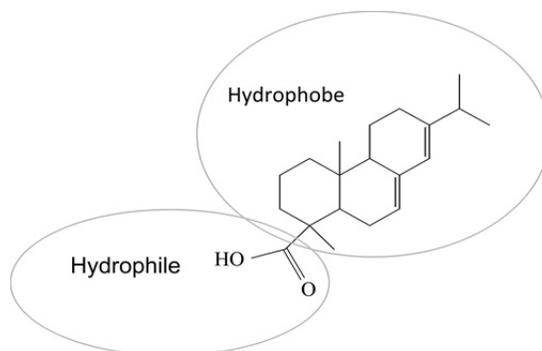


Figure 4. Structure of a Rosin Acid

Typically, tackifiers have been blended in acrylic adhesives in the range of 20% to 40% level (percent solids on solids). In times when tackifiers are relatively inexpensive and in good supply, there are few issues with this strategy. However, if tackifier supply is stressed, then one may wish to use them more judiciously and place the tackifier where it would have the most impact. Thus, it would be highly desirable to enrich just the surface of an adhesive with tackifier and

adjust the rheology of the balance of the adhesive to optimize performance. In principal, the simplest approach could be to coat a thin layer of a tackified acrylic on top of an un-tackified acrylic. However, recall that tackifiers are low molecular weight species that have the potential to move around in soft matrices.

To illustrate this point, a thin layer of neat tackifier was coated on top of an acrylic PSA. The reason a neat tackifier was chosen is that its presence at the surface is readily detectable as a hazy layer and the surface tack is near zero. Aging this construction over time causes a dramatic change in properties. The left side of Figure 5 shows a sample when it is first coated on PET film with a base of 0.8 mil of an acrylic adhesive and top coated with 0.1 mil of neat tackifier. The sample was placed against a black background in order to provide good contrast. When the sample is merely placed in a 50°C oven for five minutes, it clears and becomes very tacky at the surface. At this point, the tackifier has mixed into the balance of the adhesive even after this short duration of time. Hence, the tackifier content at the surface is declining with time.

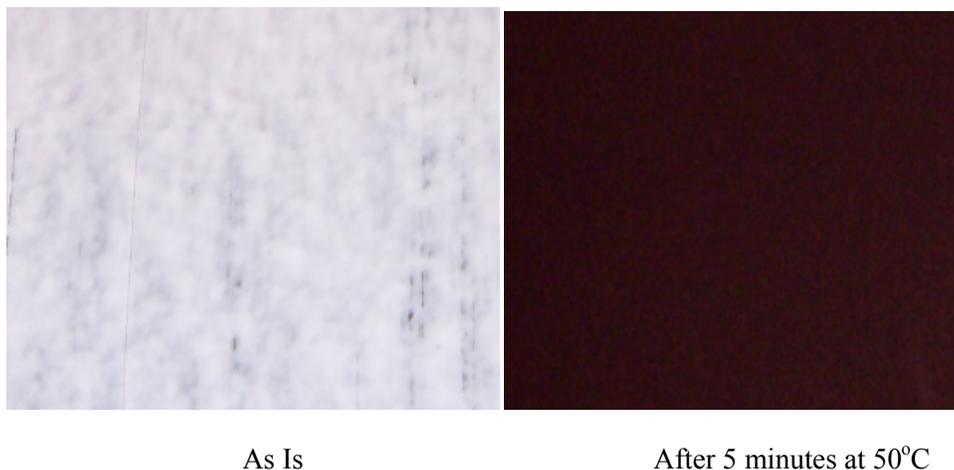


Figure 5. Tackifier Top Coat on an Acrylic Adhesive

Simply enriching tackifier in the top layer and having no tackifier in the bottom layer creates the same problem. Over time, the tackifier will equilibrate between the layers and any surface enrichment in the top layer is lost. So if tackifiers are to be used in the top layer, a mechanism has to be devised where they remain in that layer. Not all tackifiers are compatible with acrylic adhesives. Certain aliphatic hydrocarbon based chemistries are a prime example. So if such a tackifier is used in the top layer, thermodynamically, it will have little, if any, migration into acrylic adhesives. On the other hand, these tackifiers are very compatible in many hydrocarbon-based resins such as olefinic resins, isoprene, and butadienes. Hence, one possible solution is to coat a tackified hydrocarbon on top of an acrylic adhesive. In Table 4, the PSA performance is summarized for two acrylic adhesives “as is” and the same acrylic adhesives with 0.1 mils of a

tackified hydrocarbon top coat layer cast from an emulsion. The overall coating thickness of all of the samples is 0.9 mils.

Table 4. Effect of Tackifier Enrichment at the Surface

	# of Layers	HDPE Peel (N/in)	SS Shear (hr) 1"x1"x1kg	% Tackifier in Composite
Tackified Acrylic	1	5.0 A	15	27%
Low Shear Acrylic	1	3.9 A	5	0%
Low Shear Acrylic + Top Coat Layer	2	5.4 A	5	6%
High Shear Acrylic	1	1.2 A	>50	0%
High Shear Acrylic + Top Coat Layer	2	4.1 A	>50	6%
Blend: 89% High Shear Acrylic/11% Top Coat	1	1.4 A	>50	6%

Clearly, the addition of a top coat layer significantly improves polyolefin adhesion without a detrimental loss of shear while minimizing the use of tackifier. Also, the effects of both rheology and surface energy manifest themselves. If there is no low surface energy top coat layer, the HDPE peel numbers are lower. In order to match the properties of a tackified acrylic, the rheology of the bulk of the adhesive, that is, the base coat has to match the rheology of the tackified product. Thus, using a lower modulus adhesive (Low Shear Acrylic) as a base coat better matches the tackifier acrylic.

If the tackifier is compatible in both layers, then peel stability is less stable. To demonstrate this, HDPE peels were measured after 20 minute dwells for freshly made samples as well as those which have been aged at 50°C for one week and then equilibrated at standard PSTC conditions (23 ± 1°C and 50 ± 2% relative humidity) overnight. The all acrylic construction dropped over 20% while the more heterogeneous composition was stable.

Table 5. Aging of Double Constructions

HDPE Peel (N/in)	Initial	Aged
Low Shear Acrylic with Tackified Acrylic Top Coat Layer	6.6 A	5.3 A
Low Shear Acrylic with Tackified Hydrocarbon Top Coat Layer	5.8 A	6.0 A

Coating Double Label Constructions

Commercially, it is extremely difficult to coat a pressure sensitive adhesive, rewind it, and then apply a second layer as a top coat. The preferred method is to use a multilayer coating technique such as a slide coater, curtain coater, or slot die coater. These approaches have been established for years, but presently only have limited use in the pressure sensitive adhesives industry owing to limited constructions that require them. For example, in a slide coater (Figure 6), one adhesive simply flows over a second as it flows down the “slide.”

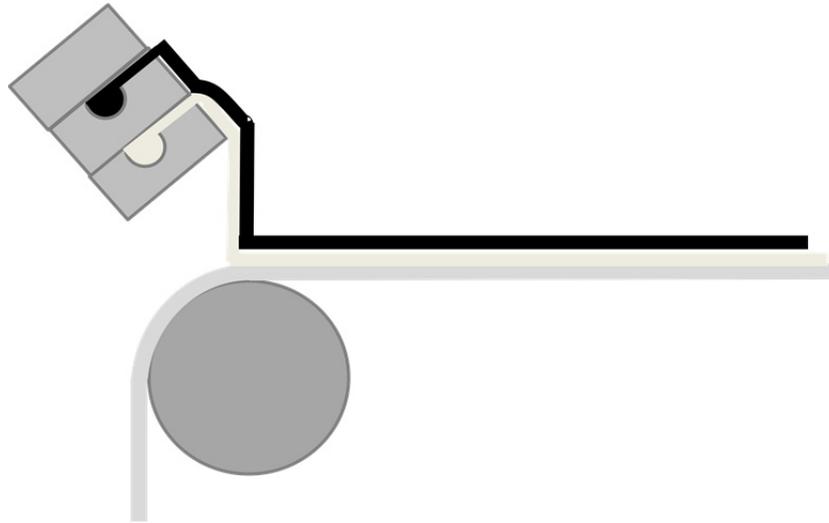


Figure 6. Two Layer Slide Coater

Although this adds some complexity, there are also additional potential advantages. For example, the solids of acrylic emulsions can be higher than the highest solids tackifiers that are commercially available. Since there is no tackifier in the base coat, this would permit coating an overall higher solids emulsion than is feasible if a tackifier had to be blended into entire adhesive. In addition, there is more formulation flexibility for coatability. Surfactants that are used for the very aggressive wetting of release liner that is required in curtain and slide coating can be limited to the layer that comes in contact with the release liner. This also has the potential to improve PSA properties and reduce cost.

Conclusion

The addition of tackifiers to pressure sensitive adhesives is a well-known means of optimizing performance. Whenever tackifiers are relatively inexpensive and in good supply, the most cost-effective formulations for acrylic PSAs are to simply blend tackifiers and acrylics. However, if tackifier supply is a concern, a more cost-effective solution may be to prepare a two-layer construction. A layer against the face stock would be optimized for rheological properties where the top portion would be designed to have the surface chemistry required for adhesion to the targeted substrates.

References

1. Wood, Timothy G.; The Effects of Tackification on Waterborne Acrylic PSA's; Adhesives Age, Jul. 1997, pp. 19-23

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