Waterborne Pressure Sensitive Adhesives

Introduction
Pressure sensitive adhesives, PSAs, are applied to labels, tapes and films to adhere to a variety of substrates with varying degrees of permanence. These are used in industrial, consumer and medical applications to name a few. Strength and tack are the key elements of the adhesive performance while the viscosity affects the applied film thickness. The apparent adhesion of a material is the combined cohesive and adhesive properties of the material. Each must be balanced to obtain the final desired properties. Poor adhesive or cohesive properties may result in early failure of the adhesive. Fumed silica enhances the cohesive properties of the film thus building a more integrated bond line.

Fumed silica has long been used in adhesives and sealants to provide thixotropy and reinforcement. Fumed silica is amorphous silica that through its structure of aggregated particles reduces the flow properties of a fluid. This property results in an increase in viscosity, reduced flow and leveling, and reduced sag. By replacing more traditional thickeners, such as cellulosics, associate thickeners and clays, viscosity can still be maintained, but with the added benefit of reinforcement. The same structure that controls viscosity response also sets up an internal network of inorganic particles that improve the bulk properties of the dried film.

Commercially available fumed silica is offered as either a powder or liquid dispersion, most often as an aqueous blend. Powders are offered in hydrophilic and hydrophobic grades. Treatment of the surface offers some unique features to the product. Hydrophobic fumed silicas are offered in a range of hydrophobicity depending on the treatment type. Also available are fumed silica dispersions that offer the formulator the ability to skip the dispersion phase associated with fumed silica powders. Replacing a powder with a dispersion still results in the combined properties of reinforcement and viscosity.

Two common generic types of PSA are waterborne and hot melt which were included in this study. Waterborne systems are very often based on copolymers of acrylates and vinyl acetate ethylene. Properties such as glass transition point ($T_g$), particle size and distribution, and toluene-insoluble content are chosen along with additives such as plasticizers, tackifier resins and surfactants to achieve the ultimate desired performance. Hot melts are comprised of rubber, tackifier resin and antioxidants. These products are compounded at elevated temperatures, typically 120° to 175°C, applied at these temperatures, and allowed to cool to achieve their final properties. For strength reasons, styrene block copolymers are often chosen as the base polymer. Over the last forty years, these polymers have offered the combined adhesive properties of styrene with the flexibility of butadiene, isoprene, and ethylene-butylene. Natural and synthetic resins are added to modify these blocks to achieve specific formulating requirements.

Testing Protocol
The Pressure Sensitive Tape Council (PSTC) publishes various test methods for PSAs. Of these, three are often used to evaluate the properties of the adhesive, PSTC-101 International Standard for Peel Adhesion of Pressure Sensitive Tape, PSTC-107 International Standard for Shear Adhesion of Pressure adhesive, PSTC-107 International Standard for Shear Adhesion of Pressure adhesive.
Sensitive Tape, and PSTC-16 Loop Tack. A Brookfield Viscometer may be used to measure the impact of the fumed silica on viscosity. Thermal stability testing was also conducted on various formulations using ASTM International D4499 Standard Test Method for Heat Stability of Hot-Melt Adhesives.

These tests are used to compare the performance of various types and levels of fumed metal oxides produced by Evonik. Peel adhesion is perhaps the only true adhesive test in this set. The tests for shear adhesion and loop tack are more indications of the flow characteristics of the adhesive film. The ability of the system to flow and wet the substrate as well as its resistance to deformation has more of an impact on the results of these test methods.

Waterborne PSA Study

180° Shear Adhesion Results

Acrylic latex and two vinyl acetate-ethylene copolymers (ACR-1, VAE-1 and VAE-2) were evaluated. Fumed silica improves shear strength of adhesives by increasing the cohesive properties of the film. As with any shear adhesion test, the total force is a sum of adhesive and cohesive properties. The three latexes were tested with the PSTC method’s arrangement of a ½ inch x ½ inch x 1000 gram configuration on stainless steel panels.

Shear adhesion for ACR-1 improved when using both the powder and dispersed form of fumed silica. The improvement was more pronounced when using 200 SA hydrophilic dispersion instead of the powder.

VAE-1 also shows an improvement in 180° Shear times with the dispersion. In this case, the 200 SA hydrophilic powder begins to detract from adhesion. This may be due to a number of factors including shear sensitivity of the emulsion.

VAE-2 also shows improvement for both dispersion and powder forms of fumed silica.

![Figure 1. ACR-1 Shear Strength (minutes)](image)

![Figure 2. VAE-1 Shear Strength (minutes)](image)
Adhesion-in-peel Results
Adhesion-in-peel is related to both the adhesive properties of the film, but also the cohesive. Formulation changes that negatively affect the tack properties (see below) can also affect the adhesive properties. However, the addition of a fumed silica improving shear (see above) can balance these properties out.

ACR-1 is intended for clear decal applications. One application is for screen-printed signs for the side of trucks. Clarity is obviously important, as is strength to prevent peeling. 200 SA hydrophilic dispersion results in better retention of inherent adhesive properties when tested in peel than 200 SA hydrophilic powder.
VAE-1 was also designed for clear label applications. Use of 200 SA hydrophilic powder shows a slightly faster decrease in peel adhesion, over the dispersion. Loading levels should be kept at 1% to 2% dry/dry loading.

Finally, VAE-2 was also tested. This is a general purpose adhesive designed for paper and label applications. For this latex, the powder and dispersion had very similar responses.

Figure 5. VAE-1 Adhesion-in-Peel (N/10mm)

Figure 6. VAE-2 Adhesion-in-Peel (N/10mm)
**Loop Tack**

The addition of any powder into a PSA film has the potential for severely impacting the tack. It is not unusual for formulators to use clay, calcium carbonate and other natural fillers. Additionally, precipitated silica and fumed silica may be added to control the tack of a PSA.

In this study, the ACR-1 shows only a moderate drop in tack with the dispersion over the full range of loading tested. The powder begins to show a significant loss of tack at higher loading levels.

![Figure 7. ACR-1 Loop Tack (N/10 mm)](image)

With VAE-1, the loss of tack for both materials was about even with a slight advantage to the dispersion.

![Figure 8. VAE-1 Loop Tack (N/10 mm)](image)

The overall tack trend line remained nearly constant over the range of silica loading for both powder and dispersion in the VAE-2 formulation.
Conclusions for Use in Waterborne PSAs
In pressure sensitive adhesives, the use of fumed silica dispersion is generally better than using the equivalent fumed silica powder. Both products have a significant impact in improvement of shear strength while having moderate or little impact on other PSA tests. The results also indicate that each lattice must be studied as results may vary. While improving shear results, fumed silica does diminish the loop tack and adhesion-in-peel results so care must be taken when these properties are important.

Hot Melt PSAs

Raw Materials
Typically, hot melt adhesive formulations are comprised of various combinations of synthetic rubber(s), natural resin(s), synthetic resin(s), oils, plasticizers, and antioxidants to achieve properties based on the specific application.

Synthetic Rubber
A common type of synthetic rubber used in hot melt adhesives requiring higher performance is styrene block copolymers. This type of synthetic rubber is made through a closely controlled polymerization step to form blocks of specific monomers. Two types of monomers are chosen based on their glass transition temperature ($T_g$). Styrene is typically chosen as the higher $T_g$ monomer that has more affect on the adhesive properties, while a variety of lower $T_g$ monomers are chosen and which affect the cohesive properties. These polymers are typically sold as “diblocks”, in which two different monomers form discrete blocks; as various forms of “triblocks” usually with the harder, high $T_g$ monomer on the ends of the polymer chain and a more flexible chain in the middle; or as blends of “diblocks” and “triblocks” to balance performance properties. Other structures are possible and the formulator should consult suppliers of these materials for further information.
Two styrene block copolymers were used in the evaluations. The first, SBC-1, is a linear block copolymer of styrene and isoprene with 15% total styrene content and 19% diblock. The diblock is mobile enough to provide improved surface wetting and tack. The second, SBC-2, is also a styrene and isoprene copolymer with 16% total styrene but with 55% diblock for improved tack.

**Natural and Synthetic Resins, and Oils**

Organic resins added to hot melt adhesive formulations modify the properties of the rubber, such as strength and tack. These are typically chosen based on their melting or softening point, color, thermal stability, etc. As a general guideline, higher melt point resins enhance the properties of the styrene block, while lower melt point resins the softer segment, in this study isoprene.

In this study, several resins and oils were evaluated. Among these, the higher melt point materials were used. RES-1 is a polyterpene tackifier with a Ring and Ball softening point of 85 °C. RES-2 is an aliphatic C5 resin with a Ring and Ball softening point of 94 °C. Both products modify the styrene portion of the SIS polymer. RES-3 is a liquid hydrocarbon resin with a Ring and Ball softening point of 5 °C. This is used to increase tack and reduce viscosity. Naphthenic oil, OIL, was added and acts as a plasticizer to increases tack and reduces viscosity in a hot melt adhesive.

**Other Raw Materials**

Other raw materials such as antioxidants are added to maintain thermal stability of the hot melt adhesive. These products are used to tie up free radicals generated when high heat and oxygen are in the presence of organic materials. A sterically hindered phenol was added as a primary antioxidant, AO. This class of antioxidant reacts quickly with peroxy radicals, ROO•, to break the cycle of degradation.

**Compounding and Coating**

A one-quart sigma-blade mixer was used to compound the formulations and a hot melt laboratory coater was used to apply the adhesive to 2-mil thick biaxially oriented polyester (BOP) film. The coater was adjusted to achieve coat weights of 20 to 25 g/m². Formulations were made, coated and tested within one week.

The resin and antioxidant were added to the mixer and the resin was allowed to melt. The styrene block copolymer was added and allowed to melt before the liquid hydrocarbon resin or oil was added. This was mixed to an even consistency before any fumed silica was added. It is necessary to do this as may coat a partially melted resin mass and interfere with the process.

**General Purpose Formulation**

Based on the available information, a model general purpose formulation was developed to evaluate various fumed silicas.

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<th>phr</th>
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<tr>
<td>RES-1</td>
<td>110.0</td>
<td>43.47</td>
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<tr>
<td>AO</td>
<td>3.0</td>
<td>1.19</td>
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<tr>
<td>SBC-1</td>
<td>100.0</td>
<td>39.53</td>
</tr>
<tr>
<td>RES-3</td>
<td>40.0</td>
<td>15.81</td>
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As mentioned, the properties of Loop Tack and 180° Shear Adhesion are more related to the flow properties of the adhesive. These are both tested at room temperature conditions. Results of the test should indicate if the fumed silica has a more positive impact on the resistance to flow during removal than during the wetting. This would be an improvement when trying to improve the permanency of the adhesive bond.

Six fumed silica products were evaluated in this study. Two, 150 and 200, are hydrophilic fumed silicas with BET Surface Areas of 150 m²/g and 200 m²/g. Four surface treated fumed silicas, ST-1 through ST-4, have various surface areas and treatments. ST-1 is a silicone oil treated fumed silica; ST-2 is treated with octylsilane; ST-3 and ST-4 are treated with dimethyldichlorosilane with surface areas of 130 m²/g and 200 m²/g respectively.

With the exception of 3.0% loading of ST-1, the addition of fumed silica increases the loop tack properties of the system. In this test, the 1.5% loading of ST-3 proved to show the greatest increase in loop tack.

**Figure 10.** Loop Tack (N/10 mm) of Hot Melt with Various Silicas
With the exception of the 1.5% loading of 200 SA hydrophilic, the 180° Shear results were higher. The largest increase in Shear results is seen in the 3.0% loading of ST-2.

As adhesion in peel is more of a true adhesion test, a comparison of the results indicates that these properties are improved by fumed silica addition. The largest increase in this property is seen in the 1.5% loading level of ST-3.
Overall, the use of fumed silica has shown no significant detraction from the adhesive properties. However, the addition of fumed silica may increase the viscosity of the system. A comparison of the viscosity at 350 °F (177 °C) was made. A Brookfield HA head with a SC4-21 spindle was used at 5 rpm.

![Viscosity Chart]

**Figure 13.** Melt Viscosities with Various Silicas

All loading levels at 1.5% showed no significant change in viscosity. The error of the test is ± 2,000 cPs. Loading levels of 3.0% fumed silica showed a significant increase in viscosity.

**Thermal Stability**

The viscosity stability of a hot melt adhesive maintained at operating temperature is an indication of the usable life of the adhesive when kept at high temperatures. ASTM International D4499 *Standard Test Method for Heat Stability of Hot-Melt Adhesives* was used to determine the melt viscosity at 24, 48 and 72 hours and compared to the starting, time zero ($t_0$), viscosity.

In this study, a more typical label formulation was used. This is made up of the following:

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<tr>
<td>SBC-2</td>
<td>100.0</td>
<td>35.0</td>
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<tr>
<td>RES-2</td>
<td>142.9</td>
<td>50.0</td>
</tr>
<tr>
<td>OIL</td>
<td>42.9</td>
<td>15</td>
</tr>
</tbody>
</table>

**Table 2.** Hot Melt Label Base Formulation
The antioxidant used above, AO, was compared to two fumed metal oxides, FMO-1 and FMO-2, for thermal stability and were added at 0.5 phr loading level. Sample specimens were kept at 177 °C (350 °F) and viscosity was tested at 24, 48 and 72 hours and compared to the initial viscosity. A plot of the results is shown on the chart.

![Heat Stability](chart)

**Figure 14.** Heat Stability (pct init. visc.)

The initial viscosity of each material was approximately 20,000 cPs indicating that the fumed metal oxides FMO-1 and FMO-2 do not have a significant affect on rheology.

**Conclusions for Hot Melt PSAs**

The use of fumed silica and fumed metal oxides offer the formulator a number of options in formulating hot melt adhesives. The choice and loading level can positively affect the properties typically studied. The use of fumed metal oxide products can also enhance the pot life of these adhesives thus extending time between costly cleanups.
Appendix – Standards Organizations

ASTM International
100 Barr Harbor Drive
P.O. Box C700
West Conshohocken PA  19428

Pressure Sensitive Tape Council (PSTC)
P.O. Box 609
Northbrook IL  60065
TECH 32 Technical Seminar Speaker

Fumed Silica Use in Pressure Sensitive Adhesives
Rodney Conn, Evonik Degussa Corporation

Rodney Conn is an applications manager in Evonik Degussa’s Inorganic Materials Business Unit, where he is responsible for the adhesives and sealants and the polyester resins industries. He handles technical support for fumed silica and fumed oxides, precipitated silicas and carbon blacks.

Conn holds a B.S. in chemistry from the University of Akron. He started his professional career as a formulator of adhesives and sealants with Macco Adhesives, an ICI company, where he spent 10 years, followed by technical service positions at both UCAR Emulsions and Huels America. He is the Chair of ASTM C24 Committee on Building Seals and Sealants and received the Sealants Hall of Fame Award in 2003. Conn has presented papers at The Adhesion Society and ASC, has taught ASC short courses, and has been published in Adhesives Age magazine. He also holds a German patent for the synthesis of fluoroalkylsilanes.

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