Mechanically Dispersed Polymers in Pressure Sensitive Adhesives

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Introduction

Pressure sensitive adhesives are typically manufactured as solvent-borne polymers, water-borne polymers (ie, emulsions), or 100% solids polymers (hot melt adhesives or energy curables). Each type of technology has unique advantages and limitations which dictate the applications where each can be used.

Hot-melt adhesives are a common technology used in PSAs. Block copolymers of styrene with rubbery components such as isoprene or butadiene are often used in hot-melt formulations and these copolymers are typically manufactured via anionic polymerization. This limits the compositional tunability due to the limited monomers which can be used with this approach. Hot melt PSAs also suffer a disadvantage for specialty applications due to the extra time required and waste generated at adhesive changeover and when switching between different adhesive grades on the extrusion coating line. This limits their applicability in specialty applications, due to the desire to minimize startup and changeover waste. Another limitation of hot-melt adhesives has to do with the viscosity at the time of coating. Whereas water-borne and solvent-borne PSAs can flow quickly onto the web and therefore can be coated at fast line speeds and very low coat weights, the viscosity of hot melts is much higher, which places limitations on hot melt adhesives in some coat weights and constructions.

Solvent-borne polymers offer good performance in many applications due to their film formation capability and excellent water resistance compared with water-based polymers due to the inherent lack of ionic components in these processes. However, the cost and environmental impact associated with solvent removal and capture or incineration during drying are important factors which limit the applicability of solvent –borne PSAs. Certain properties, such as solids content and molecular weight, are also limited by the viscosity of the solution.

Water-borne, or emulsion, polymers are highly desirable from an environmental standpoint due to the absence of a flammable solvent. Although water-borne polymers are compositionally limited to relatively hydrophilic compositions due to the requirement to transport monomer through the aqueous phase in emulsion polymerization, this type of process offers ease of tunability that is not accessible with styrenic block copolymers (SBCs). Water-borne polymers also offer a rheology that is more suitable for lower coat weights versus hot melt polymers. Due to the tunability of the formulation, these can also be applied by a broad range of coating methods, such as, curtain, gravure, reverse gravure, and pattern coating techniques that are not accessible with hot melt polymers, which must be coated by extrusion techniques. In addition, water-borne adhesives are the only type of technology which allows blending of two distinct particles which remain as separate phases at least until the adhesive is dried but may undergo morphological changes at even higher temperatures. This opens up the possibility of heat-activated adhesives, for example.

Each of the three types of polymer technologies outlined above has benefits and limitations, which are summarized in Table 1.

Table 1: Benefits and Limitations of Various PSA Polymer Technologies

	Solvent-Borne	Water-Borne	Hot Melt
Benefits	Good film formation and water resistance; Fast line speed and low coat weights accessible	No flammable solvents; Fast line speed and low coat weights accessible; Can form blends with distinct phases; Tunable rheology profile to use on different coater heads	No flammable solvents; Block copolymers have unique elastomeric properties
Limitations	Flammable solvent must be removed; Cost	Limited to partially water-soluble monomers when emulsion polymerization is used	Difficult to achieve low coat-weights; Limited coating methods

Water-Borne Block Copolymers – The Best of Both Worlds

Synthesis of Block Copolymers in Aqueous Media

Water-borne block copolymer structures are attainable through living/controlled radical polymerization techniques such as stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP), and reversible addition fragmentation transfer (RAFT) polymerization, but the commercial viability of these approaches is limited due to cost. The practicality of conducting these techniques in aqueous media is currently limited by factors such as high temperature requirements (for ATRP), retarded kinetics (for RAFT polymerization), residual mediating agent, and added process complexity.[1] Most early work involving living/control radical polymerization techniques in aqueous media has focused on miniemulsion, which has its own limitations in terms of commercial viability due to process complexity and cost. More recently, there have been significant improvements in the corresponding emulsion processes, although commercial implementation is still limited by cost considerations.[2,3]

Block copolymer structures suitable for PSAs, such as SBCs and olefinic block copolymers (OBCs),[4] are attainable commercially using anionic living polymerization and post-metallocene catalysis, respectively, but these polymerizations are typically carried out in solvent and therefore do not inherently result in a water-based polymer, unless further processing steps are introduced.

Dispersion Technology

Traditional dispersion processes consist of phase inversion or direct emulsification.[5] With a phase inversion process, water is slowly added under shear to a mixture of polymer and surfactant. When the water reaches a critical level, the mixture inverts from a water-in-oil dispersion to an oil-in-water dispersion. With a direct emulsification process, the polymer or solid to be dispersed is first melted, then introduced to the aqueous phase under shear with a large amount of surfactant. This type of process works well with tackifiers and other low-molecular weight materials because the melting point and melt viscosity are fairly low. High-molecular weight polymers are not typically able to be dispersed using a traditional rotor-stator due to their high melt viscosity. The melting point of the polymer is also a limiting factor because it must be below the boiling point of water in a non-pressurized system. Alternative methods include grinding[6] and using solvent to aid the dispersion process.

A novel mechanical dispersion process, developed over the past several years, is a unique high shear technology that allows production of water-borne polymer dispersions that have until this point not been accessible.[7] This technology offers a solvent-free process with low levels of surfactant to disperse high-molecular weight polymers in water, producing stable dispersions at up to 60% solids with narrow particle size distributions in the sub-micron range and viscosities of > 10 cps.

Technologies Enabled by Mechanical Dispersion

The ability to achieve a high-solids, water-dispersed block copolymer could open the possibility of using water-borne technology in a number of traditionally hot-melt applications, such as heat-activated pressure-sensitive adhesives, primerless removable adhesives, cold-seal adhesives, and cohesive sealants. In this paper, we will discuss in detail our results using mechanically dispersed polymers in both heat-activated PSAs and primerless removable PSAs.

Heat-Activated PSAs

Labels which do not require a release liner, or “linerless” labels, are gaining popularity in order to reduce waste and shipping costs (Figure 1). The most widely adopted solution for linerless labels is to top-coat the label surface with a silicone release coating. This eliminates the liner stock but not the cost associated with the silicone itself. The top coating approach also does nothing to address the problems associated with the adverse impact on the appearance of a label which a topcoated silicone release layer creates. Changes to the value and supply chains would also be required with this approach, since the label stock would have to be manufactured, printed, coated with the topcoat, and then cut and dispensed. An alternative approach is to use an activatable adhesive which can be transformed from hard to tacky with heat, UV, or some other activation method.

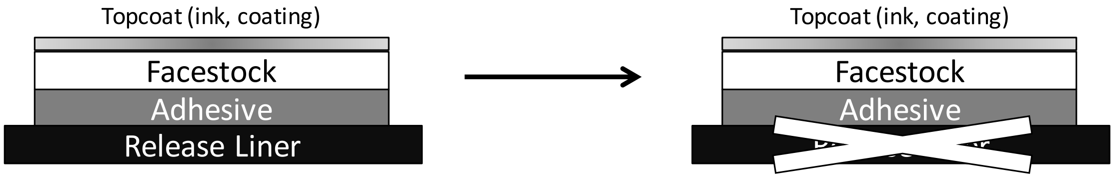

Figure 1: Structure of a Typical Pressure Sensitive Label Construction (left) and a Linerless Label With a Heat-Activated Adhesive (right).

There are several potential approaches to a heat-activated adhesive. One approach that is well known in the patent literature involves blending a dispersed polymer with a solid plasticizer (a dispersed tackifier is also commonly included in the formulations). The polymers used in this approach are widely varied, and include acrylics, styrene-acrylics, polyurethanes, and natural rubber derivatives.[8,9,10] Our unique mechanical dispersion capabilities make this approach very attractive.

Preparation of SIS Aqueous Dispersion

Dispersions were prepared on a 25 mm diameter twin screw extruder. The stabilizer was delivered by a volumetric feeder, the SIS base polymer was delivered by a loss-in-weight feeder. The stabilizer was an ethylene/acrylic acid copolymer; melt index 300 g/10 min (ASTM D1238, 190C/2.16 kg); or a long-chain primary carboxylic acid (C_{23}-C_{26} saturated aliphatic carboxylic acids). The SIS polymers were either Type

1 (triblock copolymers with 16% polymerized styrene units and 56% diblock) or Type 2 (linear block copolymer, 15% polymerized styrene units and 19% diblock). In the extruder the base polymer and stabilizer were melted, mixed and forwarded. The extruder temperature profile was set to 190°C for dispersion C, 120°C for dispersion A and B. For dispersion C, 30% wt. potassium hydroxide (CAS No. 71769-53-4) was used as the neutralizing agent, for dispersions A and B, DMEA, 2-dimethyl amino ethanol (100%) (CAS No. 108-01-0) was used as the neutralizing agent. Base and initial water were fed to the extruder at the initial water introduction point. The dilution water was fed via a second pump, and it was introduced into the dilution zone of the extruder. The resulting dispersions were cooled and filtered through a 200 micron filter. Properties of the dispersions are shown in Table 2.

Table 2: Properties of SIS Dispersions

Aqueous Dispersion	**Base Resin (g/min)**	**Stabilizing Agent (g/min / wt%)**	**Neutralizing Agent (ml/min / wt%)**	**Total Solid (wt%)**	**% Neut.**	**pH**	**Average Particle Size Diameter (⍰m)**
A	SIS Type 1 (60.5)	Ethylene-Acrylic Acid Copolymer (15.1/9.2%)	6.1 / 3.7%	46.0%	140%	9.8	2.4
B	SIS Type 2 (60.5)	Ethylene-Acrylic Acid Copolymer (15.1/7.9%)	6.1 / 3.2%	42.2%	140%	10.0	5.9
C	SIS Type 2 (41.2)	Long-Chain Primary Carboxylic Acid (3.8/2.4%)	1.0 / 0.6%	28.4%	90%	10.8	0.9

Plasticizer Selection

Four dispersed plasticizers were chosen for evaluation in this testing – identified as Plasticizers A, B, C, and D. These were chosen based on their ability to plasticize the styrene domains in the SIS block copolymer, as measured by DSC. To determine the ability of each plasticizer to depress the T_g of the styrene domains, the desired amount of plasticizer and SIS pellets (SIS with 44% styrene) were dissolved in tetrahydrofuran (THF) at room temperature by shaking for at least 48 hours. SIS with a high amount of styrene was used for the DSC experiments to give a better signal-to-noise ratio for the Tg of the styrene domains. The total solids was kept at approximately 20%, and the solutions were cast directly into DSC pans. The samples were then dried at room temperature under vacuum for at least 48 hours before making DSC measurements.

DSC data was collected on a TA Instruments Q2000 DSC with the following method sequence:

1. Equilibrate at -150 °C
2. Isothermal for 2 minutes
3. Ramp 20 °C/minute to 150 °C

4. Equilibrate at -150 °C
5. Isothermal for 2 minutes
6. Ramp 20 °C/minute to 150 °C

Each of the plasticizers were tested for plasticization by blending with SIS Type 2 polymer at concentrations of 5, 10, and 20 weight % plasticizer. As an example, the DSC curves for Plasticizer A are shown in Figure 2. A clear depression of the styrene glass transition in the SIS was seen as the amount of plasticizer was increased. In some cases, the blends of SIS with 20% plasticizer did not show a T_g for the styrene domains due to overlap with the melting endotherm of the plasticizer itself. An example of this is shown in Figure 3. A summary of the DSC results for the 4 selected plasticizers is given in Table 3.

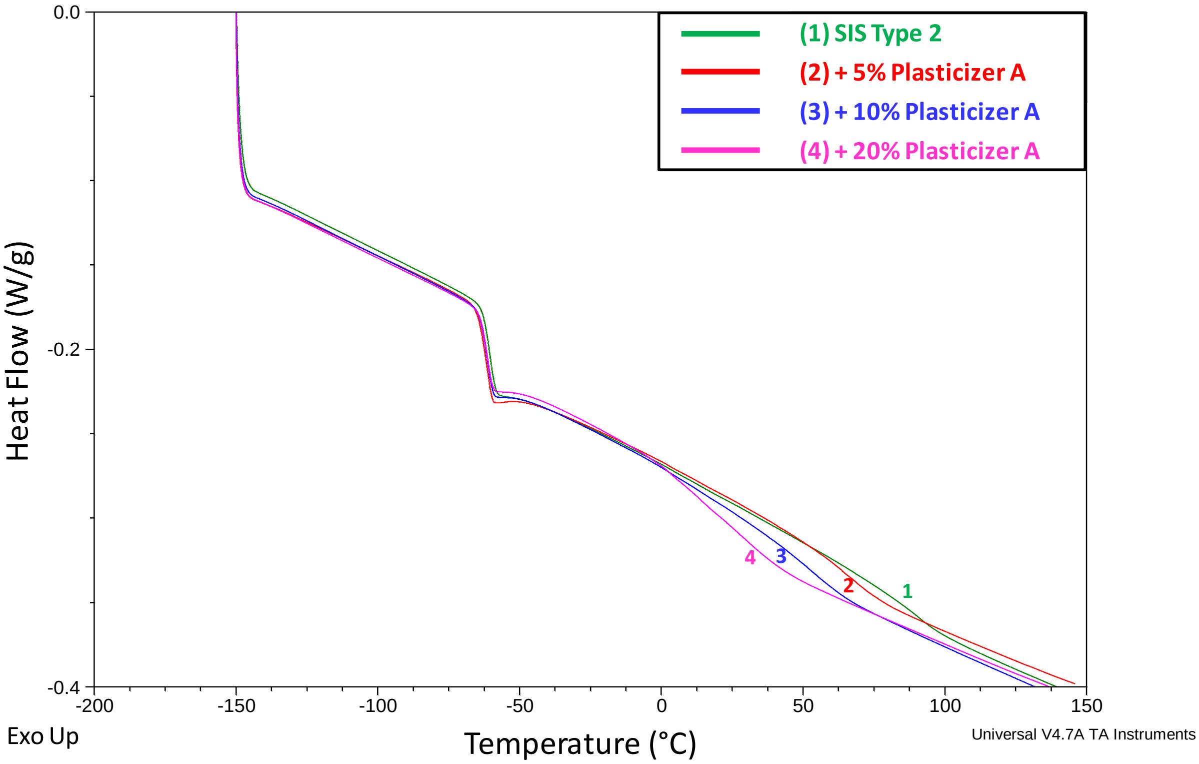

Figure 2: DSC Curves for Blends of SIS Type 2 Polymer with Plasticizer A

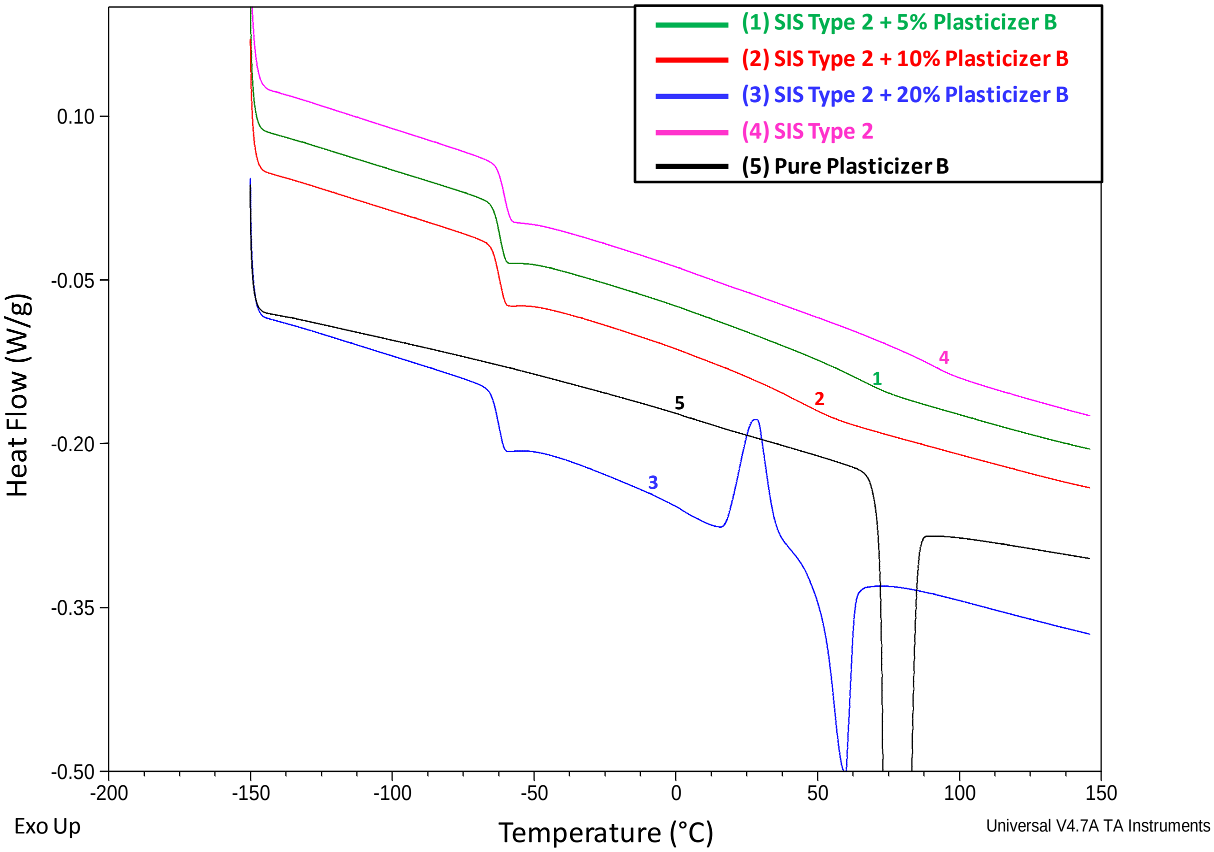

Figure 3: DSC Curves for Blends of SIS Type 2 Polymer with Plasticizer B, Indicating Overlap of Highly Plasticized T_g with Melting Endotherm of Plasticizer

Table 3: DSC Summary for Selected Plasticizers

Material	Tm (peak, °C)	ΔH_{fus} (J/g)	Tg - 5% Plasticizer (°C)	Tg - 10% Plasticizer (°C)	Tg - 20% Plasticizer (°C)
Plasticizer A	71.9	76.4	63.9	51.5	13.5
Plasticizer B	100.9	140.7	62.0	44.8	-*
Plasticizer C	70.1	11.1	61.5	68.2	63.7
Plasticizer D	65.3	99.6	68.1	59.1	37.1

*A dash (-) indicates that no polymer T_g was observed, usually due to an overlapping melting endotherm from the crystalline plasticizer.

Adhesive Formulation

To formulate the heat-activated adhesives, the three component dispersions (SIS, tackifier, and plasticizer) were weighed into a 6 dram vials in the desired ratio with a total wet weight of 20 grams. The vials were capped and shaken by hand for 30 seconds to ensure the samples were well mixed. The samples were then allowed to rest for 2 hours before being applied to a substrate (2 mil untreated oriented polypropylene). A 1.6 mil wet coating of the sample mixture was applied to the substrate with a BYK applicator bar. The coated samples were then dried in a convection oven at 50 °C for 10 minutes leaving a 0.5-0.9 mil dry film.

The dry films were placed against silicone release paper for protection and then left in a controlled temperature (72 °F) and humidity (50% RH) room overnight to equilibrate. The films were then cut into 1” by 6” strips for adhesion (peel) and blocking tests. The test strips were activated by heat using a Werner Mathis AG oven set at 110 °C for 15 seconds with the strips adhesive side up resting on a mesh shelf where the square mesh was 0.5 cm. The activated strips were immediately laminated to test substrates described below with a 2 kg hand roller. 180 degree peel force was measured after a 60 minute dwell time and 24 hour dwell time after the lamination step, using the PSTC 101 Test Method A from stainless steel (SS) panels and high density polyethylene (HDPE) panels once for each dwell time. Blocking tests used unactivated test strips and faced the adhesive towards a piece of polyester film fixed to a stainless steel panel. This construction was placed in a 50 °C oven for 1 week with a 1kg weight on top of the test strip with the resulting pressure of >=12 g/cm^2. After one week the construction was placed in a controlled temperature (72 °F) and humidity (50% RH) room overnight to equilibrate. The test strip was then subjected to the above described 180° peel force test twice in most cases since each test only uses ~2.5 inches of the construction. All formulations in the examples give wet weight fractions. Formulation details are given in Table 4 and Figure 4.

Table 4: Formulation Details for Heat-Activatable Adhesives

Formulation #	SIS Dispersion (wet wt%)	Tackifier Dispersion (wet wt%)	Plasticizer Dispersion (wet wt%)
1	65	20	15
2	55	35	10
3	35	50	15
4	75	20	5
5	45	50	5

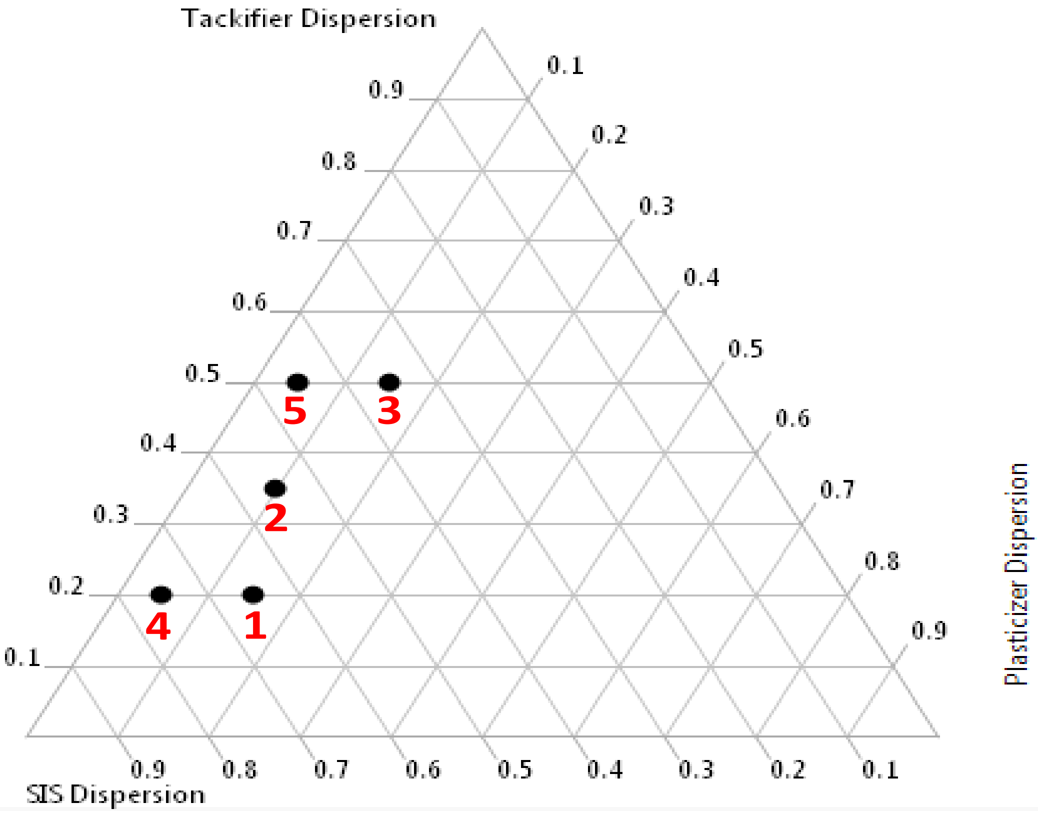

Figure 4: Experimental Mixture Design of Heat-Activatable Adhesives

Results

All possible combinations of SIS dispersions A, B, and C, as well as the four different dispersed plasticizers, were studied in the above formulations. A model was generated in statistical analysis software utilizing all of the results from these formulations, excluding samples that failed cohesively during the peel tests. Plasticizers A and D had the greatest number of cohesive failures, likely due to the greater degree of plasticization from these plasticizers, especially compared to Plasticizer C. Plasticizer type, SIS dispersion type (A, B, or C), and tackifier amount were found to be the most significant variables affecting peel. Blocking was affected by the overall formulation (SIS, Tackifier, and Plasticizer amounts), as well as the type of SIS dispersion and the choice of plasticizer. A selected summary of data is shown in Figure 5-7.

Figure 5 shows a comparison of the three SIS dispersions (A, B, and C) in a selected formulation (Formulation #5) with Plasticizer C. In this formulation, SIS “A” had the lowest peel from both HDPE and stainless steel, followed by SIS “B”, and SIS “C” had the highest peel from both substrates. SIS “C” also had the lowest blocking of all three formulations in this series. Dispersion A was made using SIS Type 1, while Dispersions B and C were made with SIS Type 2. Type 1 has a greater diblock content, and is typically used in hot-melt label adhesives. Type 2 is used more frequently in tape applications, but it is evident from Figure 5 that the two dispersions using Type 2 SIS (B and C) gave higher peel in our testing. Since Plasticizer C is not an efficient plasticizer for the SIS (Table 3), the effects seen in this series are likely attributable to the efficiency with which each polymer was dispersed. SIS Type 1 required more dispersant than Type 2. Since the dispersant is a non-tacky component, it may act as a filler and decrease the adhesion of formulations containing larger amounts, such as Dispersion “A.” Dispersions “B” and “C” were both made using SIS Type 2, but different dispersants. The long-chain primary carboxylic acid used to disperse “C” was more efficient, requiring less overall dispersant than “B,” which may have led to the higher peel values for “C.”

Figure 6 shows a comparison of the four different plasticizers in a selected formulation (Formulation #3) with a selected SIS dispersion (“C”). In this formulation, Plasticizer A had the lowest peel on both HDPE and stainless steel, followed by B, C, and D, which had the highest peel from both substrates. Plasticizer D also showed the highest blocking in this series, while Plasticizer C had very low blocking. With low blocking and the second-highest activated peel numbers, Plasticizer C seems to be the highest-performing plasticizer in this series. This may indicate that the plasticizer particles in this formulation remained separate from the polymer particles prior to activation.

Figure 7 shows the comparison of PSA performance for the five formulations with a selected SIS dispersion (“A”) and a selected plasticizer (B). Formulation was perhaps the most significant variable affecting the properties of the heat-activatable adhesive. Formulation 4 had the lowest peel from both HDPE and stainless steel, and also had the lowest amounts of both tackifier and plasticizer, which indicates that the tackifier and plasticizer play an important role in the performance of these formulations. Formulations 3 and 5 had the same amounts of tackifier, but Formulation 3 had 15% plasticizer while Formulation 5 had only 5% (Table 4). Since Formulation 3 had much higher peel from stainless steel than Formulation 5, this may indicate that the plasticizer plays an important role in forming adhesion to high surface energy substrates. This series showed less variation in blocking than some of the others, indicating that the choice of SIS dispersion and plasticizer may have a larger impact on blocking than the formulation.

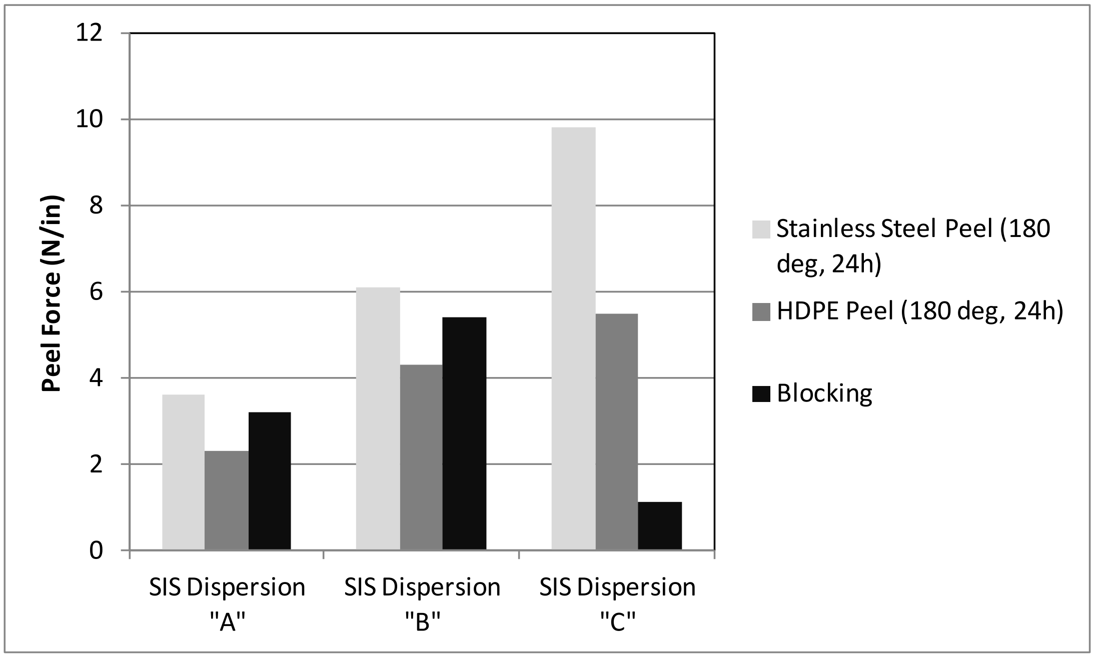

Figure 5: Comparison of PSA Performance for Three SIS Dispersions in Formulation #5 with Plasticizer C

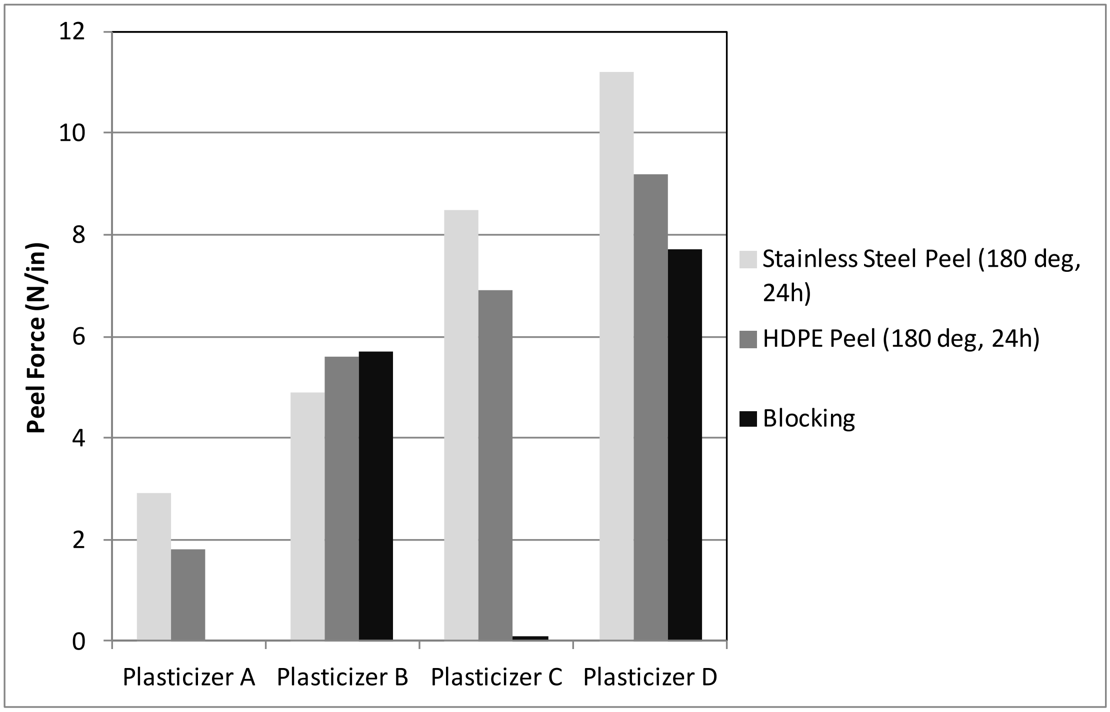

Figure 6: Comparison of PSA Performance Data for Four Plasticizers in Formulation #3 with SIS "C"

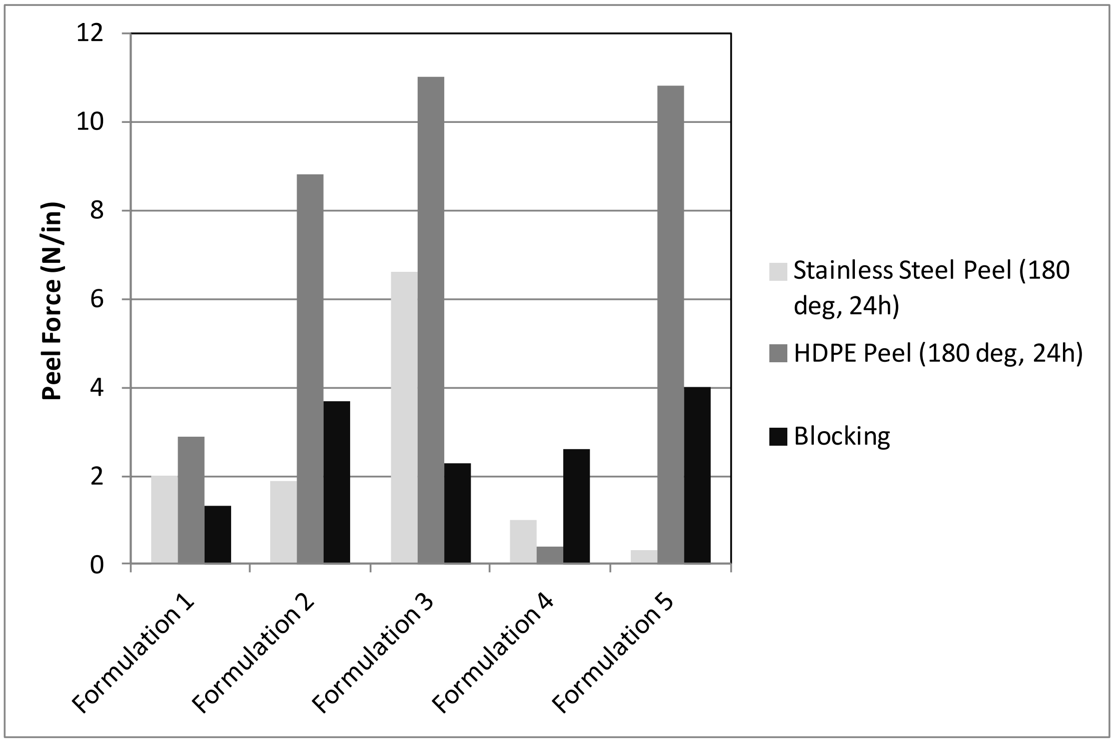

Figure 7: Comparison of PSA Performance Data for Five Formulations with SIS "A" and Plasticizer B

Primerless Removable Adhesives

Removable adhesives are applicable to a wide variety of markets, from price stickers to decorative wall decals. Requirements are low adhesion to a variety of substrates to ensure that the substrate is not damaged during removal. One drawback of removable adhesives is that the peel is often so low, the adhesive may not stick to the facestock during transfer coating. This is typically overcome by the use of a primer coating, which adds cost and complexity to the structure. Some facestocks can be purchased pre-primed with a higher-surface energy coating. Many times, a primer is coated and dried on the facestock, either in-line with the adhesive coating, or as a separate pass on the coating equipment. Historically, PSA formulations have overcome the need for a primer through addition of a crystalline wax to the adhesive.[11] Waxes are of low surface energy and low viscosity when in the molten form, and therefore should thermodynamically be driven to the surface during the drying of the adhesive. Higher levels of wax might overwhelm the surface of the adhesives to such an extent that too much adhesion would be lost. Blending a water-dispersed olefinic polymer with a traditional water-borne acrylic can enable a removable adhesive with low final adhesion due to the crystallinity of the olefinic polymer. If the melting point of the olefinic polymer is sufficiently low, it will remain amorphous for some period of time after drying, during which lamination to the facestock is enabled.[12]

Several examples of removable adhesives formulated by mixing a water-based PSA with a polyolefin dispersion are shown in Figure 8. The performance of Adhesive A (water-based acrylic PSA) with a primer was compared with the same adhesive blended with 30% of a dispersed polyolefin. Peel was measured at designated times (20 minutes, one day, and one week) on samples held at PSTC environmental test conditions. In order to accelerate aging and peel build effects, samples were placed in a 50 °C oven for one week. PSTC test method 101 was used for measuring 180° peel. Adding a hard thermoplastic filler material (dispersed polyolefin) decreased the peel of the adhesive, so a lower peel adhesive as also included as a control (Adhesive B). The sample blended with dispersed polyolefin showed good removability at all dwell times. The mechanical stability of these formulations was evaluated using a qualitative "finger rub" test. Several drops of the dispersion were placed onto an aluminum panel and rubbed vigorously in a circular motion for several seconds to expose the dispersions to a high shear rate. The samples were then qualitatively evaluated for grit. Finger rub test results are given in Table 5.

Figure 9 shows the peel and peel build performance of Adhesive A with varying amounts of dispersed polyolefin filler. By varying the amount of filler, the peel of the adhesive can be tailored for the desired application. In general, removable adhesive formulations with more filler resulted in lower peel values.

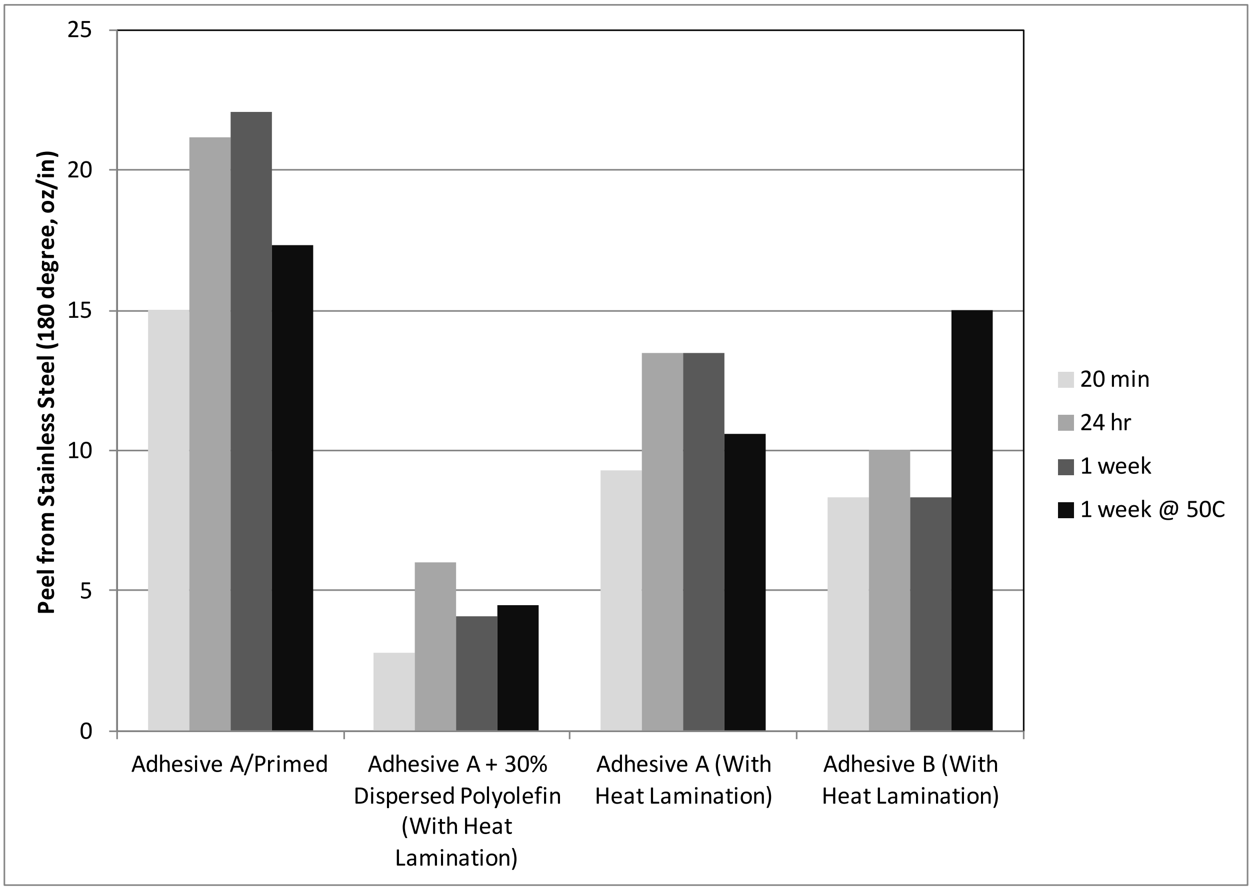

Figure 8: Peel and Peel Build of Selected Removable Adhesives

Table 5: Finger Rub Results for Selected Removable Adhesives

Adhesive	Subjective Anchorage (Measured by Finger Rub Test)
Adhesive A	1
Adhesive A + 30% Dispersed Polyolefin	4
Adhesive A/Primed	5

1 = poor, 5 = excellent

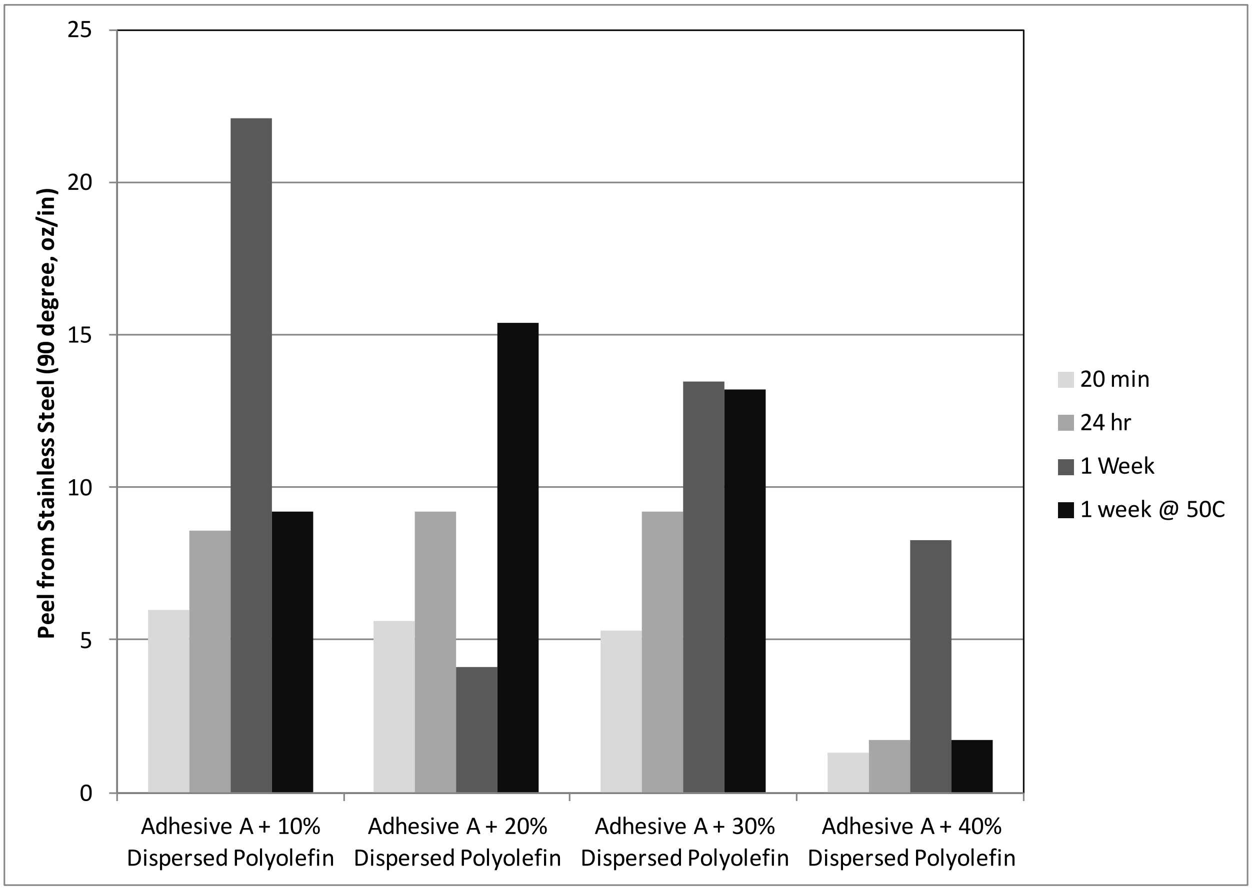

Figure 9: Peel and Peel Build of Primerless Removable Adhesives with Varying Amounts of Dispersed Polyolefin

Conclusions

Dispersing SBCs and olefinic polymers by high-shear mechanical dispersion provides a technically feasible solution in several applications, including heat-activated adhesives and primerless removable adhesives. By dispersing SIS, we have demonstrated a water-based approach in a traditionally hot-melt application. In some cases, heat-activated adhesives formulated from dispersed SBCs, tackifiers, and plasticizers exhibited good adhesion to both high- and low-surface energy substrates after adhesion as well as low blocking prior to activation. Dispersion of olefinic copolymers enabled good performance in primerless removable adhesives. By varying the amount of filler in primerless removable adhesives formulated from dispersed Olefinic polymers and traditional water-borne PSAs, a wide range of adhesion is accessible.

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