New High Solids Emulsion Polymer for Wide Temperature PSA Applications
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ABSTRACT
A new high solids emulsion polymer for pressure sensitive adhesives (PSA) applications has been developed. The high polymer content of the system (> 67%) reduces the requirement to ship and evaporate water, thus contributing to cost savings. The application temperature for this new PSA is between -45 °C and 65 °C, making it a so-called “All-Temperature” PSA. Peel and tack values of the new product are higher or at least comparable to products available in the market, but the shear values are much higher than the benchmarks. This will give advantage in processing, e.g. a better convertibility is expected.

This paper presents the results obtained from the polymeric approach used to produce an All-Temperature PSA with high solids content for low service temperatures.

I. INTRODUCTION
Water-based pressure sensitive adhesives, more specifically acrylic water-borne adhesives, find application in two important areas: tapes and labels. The latter can be divided in accordance with their adhesive properties into removable and permanent labels. In addition, permanent labels can be differentiated by the application temperature, such as freezer, refrigerator (All-Temp), and room temperature (General Purpose).

By definition, the temperature at which the labels will be affixed to a substrate is the “application temperature”, and the “service temperature” is that at which the labels will perform. Thus, general-purpose permanent PSAs are designed for application from 32 °F to 120 °F (0 °C to 49 °C), while All-Temp PSAs must allow application over a wider temperature range, -20 °F to 120 °F (-29 °C to 49 °C). The service temperature for an All-Temp adhesive, however, is the same as for a general-purpose permanent PSA, -50 °F to 150 °F (-45 °C to 65 °C). However, there is a performance difference between a general-purpose permanent PSA and an All-Temp: a general-purpose permanent PSA usually provides a higher initial tack and peel strength at room temperature.

There are several approaches in the PSA area to produce an All-Temp adhesive, namely: compounding and blending, and polymerization. The first two can produce a PSA that meets the required adhesive performance, but the product might fail to meet one or more of the following market needs:

- **Good processability**: The fast die-cutting and stripping speeds provided by acrylic water-borne PSAs that have not been modified by tackifying resins.
• **Absence of grit:** No grit formation on the coater. Grit is most often caused by the mechanical instability of the tackifier in acrylic adhesives.

• **Bleed resistance:** No bleed into paper face stocks. Bleed often occurs with adhesives made using plasticizers, as the plasticizer migrates into paper label stocks over time and at elevated temperatures.

• **FDA compliance:** Because the adhesive will be applied to food packaging, it must be compliant with USA FDA CFR 21 Section 175.105.

• **Use on paper and filmic facestocks:** Absence of grit formation is especially needed for film face stocks, since coating defects caused by the grit are more evident on these stocks.

In addition to these points, a secondary focus was placed on two important physical properties of the new polymer, namely high solids and low viscosity.

PSA raw materials and formulations with high viscosity create a number of handling and application challenges. Moreover, the industry continues to show interest in high solids polymers and coater ready adhesives. The objective of achieving a high solids content at a low viscosity has been successfully addressed by developing advanced manufacturing methods, whereby the particle size distribution is tightly controlled. The process creates populations of differently sized particles so that the smaller particles fit in the interstitial spaces created by larger particles. When the sizes of these populations are properly optimized, a lower viscosity (< 1,000 cPs) at high solids (> 67%) content results. The advantages of high solids latex are related to productivity and economic factors. Higher solids mean more polymer produced and shipped per batch. In addition, higher solids formulations mean less water must be removed, thereby reducing the energy required to reach the desired moisture content. Viewed in another way, it is possible to increase line speeds while maintaining the same dryer conditions and moisture content. Regardless of perspective, both the formulator and coater will realize cost savings and productivity improvements.

The viscosity of an adhesive formulation is highly dependent on the base polymer. Latex with low viscosity reduces the need to dilute the formulation to assure proper application. There are several benefits when producing low viscosity latex. During the polymer production, good control of the reaction temperature is an essential factor to ensure reproducible quality. This can be accomplished by having a low viscosity system that facilitates heat removal from the system during the reaction.

In addition, low viscosity latex helps to have less hold out and less mechanical stress on the material. Filtration of low viscosity polymers and formulations requires less time and pressure, giving a cleaner product. Finally, it is easier to mix and handle low viscosity ingredients in the manufacturing and compounding procedures.

In these respects, the development and introduction of high solids PSAs responds to the market trend toward high solids emulsions while eliminating the need to dilute the resulting formulation to achieve low viscosity.

The pressure-sensitive laminate industry is a highly competitive, dynamic market where innovation is rewarded with improved competitiveness and increased profits. Pressure-sensitive manufacturers continue to seek performance advancements for the facestocks, liners and adhesives used...
in the manufacture of their products. As a leading global supplier of adhesive raw materials, BASF evaluates the pressure-sensitive laminate market regularly for opportunities to provide innovative adhesive technologies that will offer the next level of performance over existing products. The pressure sensitive adhesive (PSA) market for North America is presented in Figure 1 by application. The “All-Temperature” adhesive category not only represents a significant portion of the market, but it also a technically demanding application, which presents opportunities for product improvements. Indeed, the market is demanding improvements in the following attributes of All-Temp PSAs:

- an expanded application temperature range
- a better balance of room and low temperature performance
- faster coating speeds
- better convertibility
- higher cohesion

Therefore, the objective was to develop a unique water-borne polymer with all of the required PSA attributes, with especial latex properties such as high solids and low viscosity, specifically designed to perform as an All-Temp PSA.

II. EXPERIMENTAL

Although it has been stated that in order to comply with all the requirements the development of a new polymer was the best option, the results of one more approach are presented. Thus, the approaches evaluated for the development of an All-Temp PSA were:

- Modification of standard general-purpose PSAs, by blending, and
- Polymeric approach, where new water-based polymers were specifically designed for the All-Temp PSA market.

Blending of water-borne polymers

Two latexes were evaluated as potential bases for producing an All-Temp system: a high cohesion polymer, Acronal® V-210 (BASF, T<sub>g</sub> ≈ -49 °C) which is an excellent general-purpose PSA; and a “soft” polymer, Acronal A-100 (BASF, T<sub>g</sub> ≈ -64 °C).

These polymers were evaluated neat, and as polymer blends at 25/75, 50/50, and 75/25 dry weight ratios. Adhesion and cohesion properties were measured for the substrates indicated in Table I. Peel was measured at 90°, for this particular case, at room temperature. No tackifier resins or plasticizers were used to prepare the blends. The performance was compared against the performance target values and one commercial All-Temp PSA. The results are presented and discussed in the corresponding section.

New polymer development

Some of the commercial water-borne polymers for the All-Temp market are not compounded, but based on polymers specifically designed for this application. The design implies the tailoring of the cohesive and adhesive properties by varying the polymer composition and, when solids and viscosity are target properties, the investigation of process conditions.
Several experimental designs were defined and carried out to determine the optimum polymer composition needed to accomplish the required properties. A three level factorial design was used for the first design of experiments (DOE). The content of Monomers A and B was the independent variable, and the primary monomer content was adjusted accordingly, so the total parts of monomer added up to 100. The dependent variables or responses were the properties described in Table I.

The objective of the first two designs was to narrow the composition window by finding out the trend of the adhesive and cohesive properties as a function of the independent variables. Once the composition window was narrowed, a series of "tuning" experiments was carried out until the required adhesive performance and latex properties were obtained. Process conditions were also modified during this stage to optimize the latex and PSA properties.

Testing and Performance Requirements

When developing a new PSA, different testing conditions can be used, namely: substrates, dwell time, peel angles, etc. This variety in testing is mainly due to different standards or norms, and to different customer requirements. In order to be consistent, only the properties and the indicated substrates shown in Table I were measured for the polymerization approach. These properties and substrates were considered the most typical for low temperature applications. They were used as a screening tool to decide the direction to take during the development.

In terms of performance requirements or target values for the new All-Temp PSA, different commercial products were evaluated and the maximum value for each property was used as benchmark for the All-Temp project. Table I also includes the latex target properties.

Sample Preparation and Testing

The polymers prepared were practically tested as neat. A basic compound was prepared by mixing the emulsion polymer with Lumiten® I-RA (BASF), as a wetting agent, on a wet ratio of 100/0.75. The final solids content of the system was adjusted to 60% and the viscosity to approximately 1,000-cPs with Polacryl® BR-100 (Polacryl). No pH adjustment was made, which generally was between 3.7 and 4.0.

Silicon release liner was coated at a ratio of 20-22 g/m². The coated sheet was dried at 97 °C for 2.5 min, then left at room temperature for at least 1 hr before lamination with 60# semi gloss face stock paper. After lamination, the sheets were put in a controlled temperature (72 °F) and 55% humidity room for a 24-hr conditioning before testing. Strips were cut from the sheets and tested in accordance with methods based on testing procedures from Pressure Sensitive Tape Council (PSTC). The conditions are specified in Table I. 180° Peel was tested using an Instron Model 4505. Shear was determined using a 10 Bank Shear RT-10 unit from ChemInstruments. For 180° Peel at -10 °F (-23 °C) both, the strips and substrates, were put in a cold room for 24 hr before lamination. An Imass unit, model SP-2000, was used for this test.
### Table I. All-Temp Development

**Screening Properties, Substrates, and Target Values**

<table>
<thead>
<tr>
<th>PSA Property</th>
<th>All-Temp Objective (minimum values targeted)</th>
<th>All-Temp Benchmarks (values observed)</th>
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<tbody>
<tr>
<td></td>
<td>PE Film</td>
<td>Corrugated Paper</td>
</tr>
<tr>
<td>**180° Peel @ Room Temp., lb/in **</td>
<td>&gt; 0.60</td>
<td>&gt; 1.40</td>
</tr>
<tr>
<td><strong>180° Peel @ -10 °F (-23 °C), lb/in</strong></td>
<td>&gt; 0.10</td>
<td>&gt; 1.00</td>
</tr>
<tr>
<td><strong>Shear on SS, min</strong></td>
<td><strong>½ x ½ x 500 gr.</strong></td>
<td><strong>30 min dwell</strong></td>
</tr>
<tr>
<td><strong>Latex Property</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>%Total Solids</strong></td>
<td>&gt; 65%</td>
<td></td>
</tr>
<tr>
<td><strong>Brookfield Viscosity</strong></td>
<td>@ 50 rpm, sp. #3, cPs</td>
<td>&lt; 1,000</td>
</tr>
</tbody>
</table>

### III. RESULTS

**Blends of Water-borne Polymers**

Acronal V210 shows higher adhesion and cohesive strength at room temperature than the target values, but no adhesion at -10 °F. Acronal A-100 has low shear strength and moderate adhesion at room temperature, and peel at -10 °F is reasonable. The results are shown in Figure 2. As one can see, shear and peel at 10 °F do not have a linear dependence on the blend ratio. The peel values for the blends at room temperature are almost constant and independent of the blend proportion.

Although the shear strength at room temperature of some of the blends was comparable to the target value, none of the blends showed adhesion to substrates at -10 °F. Thus, the blends could not achieve the needed combination of moderate shear strength at room temperature and adhesion at -10 °F.

**New Polymer Development**

Once it was concluded that other approaches would not produce an All-Temp PSA, the next method to evaluate was the designing of a polymer, tailored specifically for the All-Temp market. For doing this, two experimental designs were carried out having the polymer composition as independent variable.

For the first DOE, the content of monomers A and B was varied from Low (L), Medium (M), to High (H); thus, nine experiments comprised this DOE. The properties in Table I were measured for all of
these experiments. The trend of the properties as a function of the independent variables was determined using the Statistica software. The results are shown in Figures 3 through 5.

As one can see from Figure 3, the static shear is proportional to both monomers' content. Shears of 50 min or higher can be obtained at a composition window (clear area) delineated approximately by a medium to high concentration of Monomer A, at any Monomer B content.

Contrary to the results observed for shear, 180° Peel on polyethylene film (PEF), Figure 4 (top), is proportional to the concentration of Monomer A, and relatively independent of Monomer B. This creates a problem because, when comparing both figures, as the peel increases shear decreases, indicating that it will be challenging to accomplish the required cohesive-adhesive balance.

The trend in Figure 4 (top) shows that peel values higher than 0.6 lb/in (clear area) can be obtained for low to medium concentrations of Monomer A and for the whole range of Monomer B content; therefore, there is a small composition window at which both 180° Peel on PEF and shear meet the target values.

From the rest of the trends for this DOE, one can observe the following:

• From Figure 4 (bottom), 180° Peel on PEF at -10 °F decreases as both monomers' content increases. The composition at which the target value is higher than 0.1 lb/in, is at low to less than medium Monomer B content and for low to high concentrations of Monomer A.
• Figure 5 (top) shows that 180° Peel on Corrugated Paper at room temperature is above 1.4 lb/in basically for low to medium concentration of Monomer A, for all the composition range of Monomer B. It is important to mention that paper tear was observed for most of the samples tested; therefore, the observed values might be higher if paper tear had not been occurred. The same applies for this property at -10 °F.
• From Figure 5 (bottom), 180° Peel on Corrugated Paper at -10 °F will be higher than 1.0 lb/in practically for low to medium content of Monomers A and B.

From the first DOE, when one overlaps the different trends, the results show a potential composition window located at low to medium concentrations of Monomer A, and from low to below medium concentrations of Monomer B. This window is illustrated by the dark area in Figure 6 (left).

Because just four experiments from the first DOE describe this area, it was decided to further explore the region outlined by L to M content of Monomers A and B; thus, a second DOE was performed for this area. For simplicity, the response graphs for the second DOE are not shown. The second series of trends provided another composition window to study, Figure 6 (right).

The path followed to narrow the composition window is shown in Figure 7. The final composition window, Figure 7 (right), was studied extensively by a "tuning" process, until the desired performance and latex properties were achieved, represented by the dark circle.

It is important to mention that just by modifying the monomer composition it had been very difficult to attain the targeted performance. In the last stage of the development, Figure 7 (right), a combination of changing the monomer composition and process conditions was used. This combination
of independent variables produced the polymer represented by the dark circle, and whose properties and performance are shown in Table II.

This process has been scaled-up to Production Plant with both reproducible process and performance results. An evaluation of Pilot batches was performed in terms of “convertibility”. The observations are presented in the following section.

<table>
<thead>
<tr>
<th>Table II: <em>All-Temp Performance Properties</em></th>
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<tbody>
<tr>
<td><strong>PSA Property</strong></td>
</tr>
<tr>
<td>180° Peel @ RT, lb/in, 1” x 12”/min, 10 min dwell</td>
</tr>
<tr>
<td>180° Peel @ -10 °F (-23 °C), lb/in, 1” x 12”/min, 24 hr dwell</td>
</tr>
<tr>
<td>Shear on SS, min, ½ x ½ x 500 gr, 30 min dwell</td>
</tr>
<tr>
<td>Latex Property</td>
</tr>
<tr>
<td>%Total Solids</td>
</tr>
<tr>
<td>Brookfield Viscosity @ 50 rpm, sp. #3, cPs</td>
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</table>

**PT:** paper tear

*Convertibility of the new All-Temp polymer*

The performance of an All-Temperature PSA must be evaluated in terms of dry and wet adhesive properties. Important properties of the dry PSA film are the adhesion values at various temperatures and the cohesiveness (or shear), as well as the label converting properties. A critical wet adhesive property is coatability.

An evaluation of the converting properties or “convertibility” must be performed in the development process in addition to standard adhesive properties. Convertibility is a general term, which refers to a number of post-coating processes of a PSA laminate: slitting, sheeting, guillotining and die cutting/stripping. All-Temperature PSAs are low Tg (soft) polymers, which along with other properties allow them to fulfill the primary market requirement of a broad range of application temperatures. Soft adhesive compositions such as all-temp and freezer products are prone to problems during slitting and sheeting operations and in downstream operations associated with printing processes, e.g., die cutting
and stripping. These problems can be minimized, or possibly, eliminated, when the polymer system has the right balance between adhesion and cohesion.

Preliminary convertibility tests performed at industrial facilities were conducted using the new and commercial All-Temp PSA products. The focus was the evaluation of the converting performance properties of coating, slitting, die cutting, and stripping under constant process conditions, which were not forced to find a maximum or optimal value. The qualitative results showed that the new All-Temp had good convertibility. It is expected that under more demanding conditions (higher speeds, higher tensions, etc.), this good performance will be maintained, contrary to commercial All-Temp PSAs, due to the extremely high shear of the new All-Temp polymer.

**Dynamic Mechanical Analysis (DMA): PSAs comparison**

The performance of a PSA depends on its bulk properties\(^{1,2,3}\) such as molecular weight, molecular weight distribution, and \(T_g\), and on aspects influencing the adhesive-substrate interface such as polymer composition and type of substrate.

In order to study in more detail the differences in shear and peel values observed, DMA studies were performed on a general-purpose permanent (Acronal V-210, \(T_g = -49^\circ C\)), the new All-Temp polymer (\(T_g = -57^\circ C\)), a commercial All-Temp (\(T_g = -58^\circ C\)), and a “soft” polymer (Acronal A-100, \(T_g = -64^\circ C\)). The studies were carried out using a Dynamic Thermal Mechanical Analyzer with parallel plates (Aries II, Rheometric Scientific).

The storage modulus, \(G'\), and the loss modulus, \(G''\), were measured at different temperatures and frequencies. Figure 8 shows the frequency sweep for these properties at room temperature for the different PSAs. As one can see, the general purpose Acronal V-210 showed the highest \(G'\) at all frequencies, while the soft Acronal A-100 has the lowest values. \(G'\) was slightly higher for the new All-Temp when compared with the commercial one. No significant difference was observed in loss modulus \(G''\) between the All-Temp polymers.

From the \(G'\) and \(G''\) data, and using the viscoelastic window concept proposed by Chang\(^4\), the window for each of the PSAs was constructed. The main two coordinates for the window are: \(G'\) and \(G''\), both measured @ 10\(^{-2}\) rad/s and @ 10\(^{2}\) rad/s. Figure 9 presents the coordinates for each corner of the windows.

The window for the Acronal V-210 lays closer to the top right quadrant, where high shear PSAs are located\(^4\). Acronal A-100’s window is closer to the bottom left quadrant, where removable PSAs are positioned\(^4\). The windows for both All-Temp rest in between the other two viscoelastic windows, and they have practically the same coordinates, although, as one can see, the base (\(G'\) and \(G''\) @ 10\(^{-2}\) rad/s) for the new All-Temp’s window is a little bit higher.

Figure 10 presents the correlation between the static shear and their corresponding value for the base (\(G'\) @ 10\(^{-2}\) rad/s) for each PSA. The data show a good correlation between the performance and \(G'\) @ 10\(^{-2}\) rad/s. The higher the \(G'\), the higher the shear. When comparing the base of the window for both All-Temps, one can see how a small difference in \(G'\) @ 10\(^{-2}\) rad/s can affect the shear value.

Chang\(^5\) found a direct correlation between peel and the \(G''/G'\) ratio, measured at the debonding and bonding frequencies, respectively. A peel rate of 12 in/min has been found\(^6\) to correspond to a
debonding frequency of 435 rad/sec. For the bonding process, he suggested that it takes place at around 1 rad/sec. Figure 11 (top) presents 180° Peel on PEF at room temperature, as a function of the G''/G’ ratio determined at the indicated frequencies. As one can see, no direct correlation between peel and G''/G’ ratio was found for the PSAs studied. The results indicate that other molecular parameters, such as gel content and Tg, played an important role on the adhesive properties. Figure 11 (bottom) shows the dependence of 180° Peel on PEF at -10 °F on G’ measured at 1 rad/sec and -10 °F. The storage modulus G’ has been related with bonding, while the loss modulus G” with the debonding process, thus, the higher G’, the poorer the bonding process. The G’ value for Acronal V-210 was the highest one, leading to no adhesion onto polyethylene film, while Acronal A-100 had the lowest value and highest peel.

IV. SUMMARY

• Previous efforts have shown that the compounding approach did not yield the required performance. This approach has provided formulations with satisfactory adhesion performance, but were not sufficient for bleed resistance, absence of grit and/or FDA compliance.
• The latex blending approach has produced some blends (25/75-wt% soft/hard) whose cohesive-adhesive performance is adequate at room temperature, but showed no adhesion at -10 °F.
• The development of a new polymer has been the suitable method to produce water-borne polymers that satisfy the All-Temp PSA requirements, besides producing latex with unique characteristics such as high solids and low viscosity.
• Design of experiments helped to narrow the polymer composition range at which the adhesive properties were at or above the target value.
• Dynamical Mechanical Analysis showed very important details of the PSAs studied. In general, the results showed subtle but important differences between the two All-Temp PSAs, and significant contrasts with both the general purpose Acronal V-210 and the soft Acronal A-100.
• Some of the adhesive properties could not be explained just by the DMA data, thus, further characterization of the PSAs is being conducted.
• The potential advantages of having a better cohesive-adhesive balance are shown in Table III.
Table III: Typical Performance and Latex Properties for the New All-Temp Polymer

<table>
<thead>
<tr>
<th>Property</th>
<th>Market Standard</th>
<th>New All-Temp</th>
<th>Advantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shear, min</td>
<td>25</td>
<td>100</td>
<td>Better convertibility</td>
</tr>
<tr>
<td>180° Peel @ RT</td>
<td>PEF</td>
<td>0.50</td>
<td>Higher cohesion without sacrificing adhesion:</td>
</tr>
<tr>
<td>lb/in</td>
<td>C. Paper</td>
<td>1.12 PT</td>
<td><strong>better balanced system</strong></td>
</tr>
<tr>
<td>180° Peel @ -10</td>
<td>PEF</td>
<td>0.06</td>
<td>Broader performance range: 10 °F (-23 °C)</td>
</tr>
<tr>
<td>°F, lb/in</td>
<td>C. Paper</td>
<td>1.20 PT</td>
<td>to 122 °F (50 °C)</td>
</tr>
<tr>
<td>%TS</td>
<td>55.0</td>
<td>68.0</td>
<td>Higher productivity</td>
</tr>
<tr>
<td>Brookfield Viscosity, cPs</td>
<td>&lt; 1,000</td>
<td>&lt; 1,000</td>
<td>Less energy consumption</td>
</tr>
<tr>
<td>@ 50 rpm, spindle. # 3</td>
<td></td>
<td></td>
<td>Faster coating speeds</td>
</tr>
</tbody>
</table>

PT: paper tear

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The authors would like to thank Mr. Peter Ervay for performing the All-Temp reactions, Mr. Gordon Oji and Mr. Anthony H. Do for testing the PSA’s samples under very harsh conditions, Mr. Anthony Robinson for the DMA data, and the people from the Dispersions Plant in Altamira, Mexico, for their support during the scale-up of the new All-Temp.
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Figure 4: 1st Design of Experiments, 180° Peel on polyethylene film as a function of Monomer A and Monomer B content at room temperature (Top); at -10 °F (bottom).
Figure 5: 1st Design of Experiments, 180° Peel on Corrugated Paper as a function of Monomer A and Monomer B content at room temperature (Top); at -10 °F (Bottom).
Figure 6: Performance Window Summary. 1st Design of Experiments (left), 2nd Design of Experiments (right).
Figure 7: Composition Windows. 1st Design of Experiments, left; 2nd Design of Experiments, middle; "Tuning" process, right; Optimum Monomer Composition, circle.
Figure 8: (Top) Storage Modulus and (bottom) Loss Modulus as a function of frequency at room temperature for different Pressure Sensitive Adhesives.
Figure 9: Viscoelastic Window for Different Pressure Sensitive Adhesives at room temperature.
**Figure 10:** Shear as a function of storage modulus, $G'$ ($10^2$ rad/sec), at room temperature.
Figure 11: Dependence of 180° Peel on polyethylene film at room temperature on the $G''/G'$ ratio (top). Dependence of 180° Peel on polyethylene film at -10 °F on $G'$ (bottom).
REFERENCES