

Accelerated Waterborne Pressure Sensitive Adhesive Development through Rheological Screening

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Abstract

Improved quantitative test methods to guide the development of waterborne pressure sensitive adhesives (PSA) would significantly improve development quality and speed. Current limitations are due to challenging sample preparation, large potential measurement error and considerable sample test time. This paper highlights the use of rheological techniques to specifically identify discrete waterborne PSA attributes, such as high tack or shear resistance, and design PSA chemistry using rheology-based models to more quickly achieve a product with the desired balance of PSA performance properties. The effects of monomer type, chain transfer agent concentration and addition method were studied in a generic PSA composition. PSA performance was determined both by FINAT test methods for loop tack, 180° peel adhesion and shear resistance and by linear viscoelastic analysis using a rheometer. Bulk viscoelastic behavior correlates well with the measured tack and shear values and provides a better understanding of the influence of formulation variables on PSA properties. Additional modeling is required to correlate peel adhesion tests between FINAT testing and linear viscoelastic analysis.

Introduction

Water-based pressure sensitive adhesives (PSAs) are viscoelastic materials commonly utilized for labels and tapes, among other applications. Basic PSA performance attributes such as tack, peel and shear depend on the polymer's bulk linear viscoelastic properties.^{1,2} Moreover, correlations exist between adhesion test time scales and polymer deformation frequencies, with tack, peel and shear test time scales spanning the frequency range 10^{-2} to 10^2 rad/s.^{1,2} Chang used this frequency range coupled with PSA storage (G') and loss (G'') moduli to define so-called viscoelastic windows, wherein a given PSA's window provides insight into its performance properties and the type of PSA (e.g., removable, general purpose, etc.).^{1,2}

This relationship between PSA viscoelastic behavior at given frequencies and performance is useful as a means to target PSA performance attributes and application fit. Standard adhesive application tests like tack, peel and shear can be time consuming and highly dependent on film thickness and quality, which can lead to high variability in the test results (particularly with shear resistance testing). However, using rheology to probe PSA viscoelastic behavior is much less time consuming, more repeatable and more representative of in-use performance. Rheology enables one to screen samples quickly and accurately identify trends for synthetic parameters (e.g., polymer composition, chain transfer agent concentration, etc.) to achieve the targeted PSA properties.

In this paper, a Box-Behnken response surface experimental design was performed to investigate effects of PSA monomer type, chain transfer agent concentration and addition method on performance properties. The former was determined by a rheometer and the latter by FINAT test methods for loop tack, 180° peel adhesion, and shear resistance. The design variables were chosen based on their known influence on PSA performance and studied at three levels. A generic waterborne PSA composition comprised of a fixed ratio of soft and hard monomers was the basis for this design. Trends in PSA performance and rheology were determined through ANOVA (analysis of variance) and response surface regression analysis using Minitab[®] Statistical Software and used to develop empirical models for predicting PSA properties. Attempts were made to develop regression models to predict PSA performance from rheology data to eliminate the need for conventional, time-consuming PSA application tests. The results of this study are being used as a first step in a series of sequential experimental designs to develop new waterborne PSAs.

Experimental Procedures

Polymer Latex Preparation

All PSA latex samples were prepared using a 3-liter, glass reactor equipped with a thermocouple, reflux condenser, feed tube inlet and a stainless steel stirrer with three 3" diameter 4-blade axial turbine impellers. All samples were made via a seeded semi-batch emulsion polymerization process at 80°C with anionic surfactant and thermal initiator. Surfactant and initiator levels were fixed for all runs and buffer was used to maintain latex pH \approx 4. The polymerization process was as follows: the monomer emulsion was fed over three hours after which the latex was held one hour before a redox package was added followed by a thirty minute hold. The latex was cooled to room temperature and filtered through a 100 μ m filter. Latex samples were stable with little to no coagulum. Target latex particle size and solid content were 400nm and 60%, respectively. PSA glass transition temperature (T_g) was determined by DSC. A 10°C/min. heating ramp was used and T_g was measured from the second heat.

PSA Film Preparation and Evaluation

All PSA samples were tested as base (neat) polymer. A wetting agent was added and samples were diluted to 55 \pm 0.5% solids to viscosity of 250cP.

PSA films were prepared by directly coating PSA latex onto 2 mil polyester, followed by drying at 90°C for 5 minutes. Dry coat weights were 20 \pm 2g/m². All tests were performed in a controlled environment of 23 \pm 1°C and 50 \pm 1% relative humidity. All data reported are the average of three individual tests, per FINAT test methods.

PSA samples for loop tack, 180° peel adhesion and shear resistance evaluations were prepared and measured according to FINAT test methods. Loop tack and 180° peel adhesion were measured on glass substrate using FINAT FTM 9 and FTM 1 test methods, respectively. Peel adhesion dwell times were 20 minutes (initial) and 24 hours. Shear resistance tests were performed using FINAT FTM 8 on stainless steel substrate.

Rheology Measurement

The viscoelastic properties of different PSA samples were measured on a TA Instruments AR-G2 rheometer at 23°C over a frequency range of 10⁻² to 10² rad/s using 20mm parallel plate geometry. The strain employed was 1%, within the linear viscoelastic region for each sample. PSA samples were tested as 20mm diameter disks with a thickness near 2 mm, prepared by drying latex in a release liner tray.

Results and Discussion

Experimental Design

A Box-Behnken response surface design was used to explore three variables known to impact waterborne PSA performance in a generic PSA system comprised of a fixed ratio of soft and hard monomers with a small amount of acid monomer. A Box-Behnken design was chosen as it is near rotatable and allows efficient estimation of first- and second-order coefficients using fewer design points than other response surface designs with the same number of factors. Variable levels were set broadly in order to compare PSA in-service performance to rheology over an extensive design space.

DOE variables were soft monomer type, chain transfer agent (CTA) concentration and CTA addition method. Soft monomer types were 2-EHA, BA and a mixture of the two, denoted as EHA/BA, while CTA concentration levels were 0.125, 0.25, and 0.5phm (parts per hundred monomer). Three different methods of CTA addition were investigated and are denoted as 1, 1.5, and 2. Pure error (lack of fit) was estimated by including replicates at 0.375phm CTA concentration, making fifteen total runs. Table 1 highlights DOE factors and levels. DOE outputs included three FINAT test methods for PSA performance: loop tack (FTM9), 180° peel adhesion (FTM1), shear resistance (FTM8) and rheology.

PSA Latex Synthesis

All PSA latex samples were produced via seeded semi-continuous emulsion polymerization at 80°C using a thermal initiator, anionic surfactant and buffer to moderate latex pH. Monomer ratios were fixed with only the soft monomer type varying by run. A redox chaser system was used to reduce residual monomer levels to <200ppm, as measured by GC chromatography. PSA latex characteristics are summarized in Table 1. All PSA latices had 60% solids content and volume-average particle sizes within 10% of the 400nm target. PSA T_g spanned a reasonably wide range from -42.8°C to -25.6°C.

Table 1. Box-Behnken Experimental Design and PSA Latex Results.

| PSA# | Soft Monomer | [CTA] | CTA Addition Method | P.S. nm | Dp ₁ ² (vol%) nm | Dp ₂ ² (vol%) nm | solids % | pH - | Tg °C |
|------|--------------|-------|---------------------|---------|--|--|----------|------|-------|
| 1 | EHA | 0.125 | 1.5 | 397 | 385 | - | 60.4 | 4.0 | -41.9 |
| 2 | EHA | 0.5 | 1.5 | 410 | 411 | - | 60.8 | 4.0 | -42.8 |
| 3 | EHA/BA | 0.125 | 1.5 | 227 | 391 (49) | 61 (51) | 60.4 | 4.4 | -33.0 |
| 4 | EHA/BA | 0.5 | 1.5 | 230 | 400 (46) | 74 (54) | 60.8 | 4.5 | -32.7 |
| 5 | BA | 0.125 | 1 | 253 | 381 (57) | 72 (43) | 60.4 | 4.1 | -25.6 |
| 6 | BA | 0.5 | 1 | 260 | 383 (52) | 103 (46) | 60.3 | 3.9 | -27.7 |
| 7 | BA | 0.125 | 2 | 240 | 383 (52) | 70 (54) | 60.2 | 4.0 | -25.8 |
| 8 | BA | 0.5 | 2 | 279 | 476 (44) | 99 (56) | 61.0 | 4.1 | -27.1 |
| 9 | EHA | 0.25 | 1 | 405 | 390 | - | 60.4 | 4.1 | -38.9 |
| 10 | EHA/BA | 0.25 | 1 | 291 | 407 (63) | 80 (37) | 60.3 | 4.2 | -31.5 |
| 11 | EHA | 0.25 | 2 | 399 | 385 | - | 60.7 | 4.3 | -40.4 |
| 12 | EHA/BA | 0.25 | 2 | 436 | 429 | - | 60.2 | 4.2 | -33.9 |
| 13 | BA | 0.25 | 1.5 | 434 | 423 | - | 60.3 | 4.0 | -28.3 |
| 14 | BA | 0.375 | 1.5 | 439 | 435 | - | 60.2 | 4.3 | -25.9 |
| 15 | BA | 0.375 | 1.5 | 434 | 426 | - | 60.1 | 4.0 | -27.7 |

¹Lower surfactant/monomer ratio. ²Particle Size Peak Diameter.

An interesting result was observed regarding particle size distributions (PSDs). All BA-containing PSAs (Table 1, PSAs 3 – 8, and 10) had bimodal latex PSD, with both large (≈ 400 nm) and small (≈ 60 to 100nm) secondary particles at nearly equal proportions (i.e., 50 vol.-%). This was due to the surfactant concentration chosen for this study. BA-containing compositions were sufficiently hydrophilic to require a lower surfactant concentration for stabilizing the large latex particles. The result was excess free surfactant leading to secondary particle nucleation and a bimodal PSD. Reducing surfactant level by nearly 30% for PSAs 12 through 15 (all BA containing) produced monomodal particle size distributions. This reduction in surfactant concentration was not anticipated to significantly impact polymer microstructure or PSA performance. This was confirmed as replicates of PSAs 12 – 15 made using the original surfactant level (i.e., that of PSAs 1 – 11) had comparable loop tack, 180° peel adhesion and shear resistance values with those of PSAs 12 – 15 at the reduced surfactant level.

PSA Performance Evaluation

FINAT test method results for loop tack, 180° peel adhesion (20 minute and 24 hour dwell) and shear resistance are summarized in Table 2. All tests were performed using base (neat) polymer and glass substrate for loop tack and 180° peel adhesion and stainless steel substrate for shear resistance. PSAs were coated onto 2 mil polyester at an average coat weight of 20 ± 2 g/m² and test strips were conditioned according to the FINAT test methods prior to testing. Shear resistance tests were performed using a 1.8kg weight to accelerate test times and provide greater differentiation.

The data in Table 2 illustrates the wide range in performance achieved by this experimental design. Loop tack varied from 4.9 to 11.1 (N), while 180° peel adhesion ranged from 5.5 to 20.0 and 8.5 to 20.2 (N/25mm) for initial (20 minute) and 24 hour dwells, respectively. Shear resistance had the widest data range, spanning 11 to 1577 minutes. Furthermore, performance results for replicate PSA samples 14 and 15 were in good agreement with each other (within standard error) with an exception being 24 hour dwell 180° peel adhesion.

PSA Rheology

Storage (G') and loss (G'') moduli at specific frequencies were used to correlate loop tack, 180° peel adhesion and shear resistance data with rheological behavior, based on Chang's viscoelastic window concept^{1,2}. For shear resistance, G' at $\omega=10^{-2}$ rad/s – hereafter denoted as G' (10^{-2}) – was used,

wherein higher G' (10^{-2}) values indicate higher shear resistance. As peel and tack measurements encompass both bonding and debonding steps, moduli were used at frequencies corresponding to each process step.^{1,2} In peel tests bonding corresponds to G' (10^{-2}) and debonding, comprising both cohesive strength and energy of dissipation terms, corresponds to G' (10^2) and G'' (10^2).^{1,2} Generally, high peel adhesion occurs with lower values at G' (10^{-2}), as lower modulus leads to higher flow and easier substrate wet-out, and higher G' (10^2) and G'' (10^2) values, i.e., greater debonding resistance. Tack tests have the same debonding frequency dependence as peel; however the bonding frequency is higher at 10^0 rad/s. Therefore G' (10^0) and G' (10^2) and G'' (10^2) were used to correspond to loop tack results. For high tack, the trend is similar to peel, requiring lower G' (10^0) values and higher moduli values at 10^2 rad/s. However, it is important to note that a proper balance of low and high frequency moduli is critical for obtaining high tack and peel. Table 2 summarizes G' and G'' values at these frequencies for each PSA.

Table 2. PSA Latex Performance Results and Bulk Viscoelastic Properties.

| PSA# | Loop Tack N | Peel (20') N/25mm | Peel (24h) N/25mm | Shear minutes | G' (10^{-2}) Pa | G' (10^0) Pa | G' (10^2) Pa | G'' (10^2) Pa |
|------|----------------|-------------------------|-------------------------|------------------|--------------------------|-----------------------|-----------------------|------------------------|
| 1 | 7.2 ± 0.9 | 8.0 ± 0.3 | 9.5 ± 0.5 | 1577 ± 390 | 1.59E+04 | 4.95E+04 | 2.13E+05 | 1.60E+05 |
| 2 | 11.1 ± 1.4 | 11.3 ± 0.3 | 17.7 ± 2.4 ¹ | 56 ± 12 | 5.17E+03 | 2.53E+04 | 1.48E+05 | 1.26E+05 |
| 3 | 8.3 ± 1.4 | 7.8 ± 0.7 | 11.9 ± 1.6 | 1000 ± 124 | 1.59E+04 | 7.21E+04 | 2.75E+05 | 1.93E+05 |
| 4 | 10.3 ± 2.6 | 9.9 ± 0.6 | 21.4 ± 1.8 ¹ | 93 ± 4 | 5.80E+03 | 3.41E+04 | 1.74E+05 | 1.32E+05 |
| 5 | 5.9 ± 2.4 | 5.5 ± 0.4 | 8.5 ± 0.5 | 841 ± 47 | 2.91E+04 | 1.20E+05 | 3.79E+05 | 2.50E+05 |
| 6 | 4.9 ± 3.1 | 11.1 ± 0.4 | 13.5 ± 0.4 | 48 ± 3 | 1.15E+04 | 7.60E+04 | 3.20E+05 | 2.20E+05 |
| 7 | 5.0 ± 1.2 | 9.6 ± 0.4 | 12.2 ± 1.0 | 147 ± 21 | 1.33E+04 | 1.02E+05 | 3.83E+05 | 2.66E+05 |
| 8 | 9.4 ± 1.3 | 12.6 ± 0.9 ¹ | 9.7 ± 1.1 ¹ | 13 ± 1 | 3.07E+02 | 2.41E+04 | 2.19E+05 | 1.77E+05 |
| 9 | 7.6 ± 2.1 | 9.6 ± 0.2 | 10.6 ± 0.3 | 179 ± 112 | 7.91E+03 | 3.84E+04 | 1.68E+05 | 1.25E+05 |
| 10 | 6.1 ± 2.1 | 8.2 ± 1.2 | 11.3 ± 0.5 | 90 ± 20 | 1.38E+04 | 7.08E+04 | 2.66E+05 | 1.83E+05 |
| 11 | 7.5 ± 2.5 | 15.8 ± 0.5 ¹ | 16.1 ± 0.3 ¹ | 11 ± 1 | 2.80E+03 | 2.71E+04 | 1.86E+05 | 1.61E+05 |
| 12 | 9.3 ± 2.5 | 20.0 ± 0.7 ¹ | 20.2 ± 0.2 ¹ | 21 ± 3 | 5.14E+03 | 3.62E+04 | 1.98E+05 | 1.55E+05 |
| 13 | 7.4 ± 1.6 | 9.9 ± 1.1 | 12.1 ± 0.1 | 119 ± 16 | 1.32E+04 | 8.12E+04 | 3.29E+05 | 2.30E+05 |
| 14 | 6.3 ± 1.1 | 10.6 ± 1.5 | 22.3 ± 4.2 ¹ | 106 ± 2 | 1.14E+04 | 7.01E+04 | 3.07E+05 | 2.21E+05 |
| 15 | 7.7 ± 2.5 | 10.9 ± 1.7 | 16.4 ± 0.3 ¹ | 93 ± 13 | 1.25E+04 | 7.34E+04 | 3.23E+05 | 2.37E+05 |

¹Cohesive Failure, all others were clean plate.

A representative plot of G' and G'' vs. angular frequency, ω (rad/s), for the 2-EHA-based PSAs, (PSAs 1, 2, 9, and 11) is shown in Figure 1. Differences in the viscoelastic behavior for this group are clearly evident. Further comparison of these curves shows that the rheological differences at the above mentioned frequencies correspond with performance test results shown in Table 2. For example, in Figure 1, PSA 1 has the highest value at G' (10^{-2}), which corresponds to shear resistance, while PSA 11 has the lowest. Comparing the measured shear resistance and G' (10^{-2}) values in Table 2, confirms PSA 1's shear resistance was the highest (1577' ± 390') and PSA11 the lowest (11' ± 1'). This same trend between shear resistance and G' (10^{-2}) data also holds true for the other PSA samples (when grouped by soft monomer type) and is clearly evident in their respective moduli vs. ω plots (not shown).

Loop tack and 180° peel adhesion, however, are more complicated because they involve two processes (bonding and debonding) making rheological trends more difficult to discern. For example, of the four PSA's in Figure 1, PSA 2 had the highest measured loop tack (11.1 ± 1.4N) and the lowest G' (10^0) value (2.53 x 10⁴ Pa), and the latter supports the former, in that the lower bonding frequency modulus the higher the expected tack. However, PSA 2's G' and G'' (10^2) values were also the lowest and next-to-lowest, respectively, suggesting it had a lower debonding resistance than the others in Figure 1. This conflicting combination of moduli makes it difficult to visually infer tack and peel trends directly from the linear viscoelastic behavior. Consequently, a more straightforward correlation between performance metrics and rheology results was made via Minitab[®] 16 Statistical Software and regression analysis.

PSA Design of Experiments

PSA performance trends were determined using Minitab® 16 Statistical Software. Response surface regression analysis was used to analyze outputs as a function of independent variables (soft monomer type, CTA concentration and CTA addition method). Box-Cox plots were used to determine the appropriate transformation to apply to response output data. Outputs included FINAT test methods for loop tack, 180° peel adhesion and shear resistance as well as rheology values of storage (G') and loss (G'') moduli at specific frequencies.

The data were analyzed to determine first- and second-order effects, i.e., main effects and interactions. Figure 2 illustrates main effects, interaction and surface plots for $\ln(\text{shear})$. A natural log transformation was used for shear data due to the wide ranging values. The main effects plot shows the output means at all levels of each variable with the center line across the plot representing the mean for all $\ln(\text{shear})$ data.

In Figure 2's main effects soft monomer plot, the trend line connecting the means at each variable is flat, indicating $\ln(\text{shear})$ was not affected by the range of soft monomers explored in this study. Trend lines for the other two variables however, are not flat, indicating these variables affect $\ln(\text{shear})$. This is not unexpected, as CTA concentration and addition method were specifically chosen as variables due to their well-known effect on shear. The slope of the trend lines between variable levels gives an indication of strength and direction of an effect. In Figure 2's CTA concentration main effects plot, the slope of the trend line moving from 0.125 to 0.250phm is steep and negative, indicating CTA concentration has a strong negative (inverse) effect on $\ln(\text{shear})$. This trend indicates the highest shear is expected to be found using the lowest CTA level, which is valid as CTA moderates polymer molecular weight and cross-linking (gel fraction). However, the strength of this effect is considerably reduced at CTA concentrations $>0.250\text{phm}$, indicated by the lower slope of the trend line across these higher CTA levels. Likewise, the CTA addition method main effects plot shows a strong negative effect on $\ln(\text{shear})$ when changing from addition method 1.5 to 2, but little difference in $\ln(\text{shear})$ observed between addition methods 1 and 1.5.

Figure 2's interaction plots, which plot means for each variable level with a fixed level of a second variable, provide further insight into the variables whose interaction affects the output response. Parallel trend lines indicate no interaction and interaction strength is indicated by the extent to which the lines deviate from parallel. Both positive and negative interactions are possible. In the soft monomer vs. CTA concentration interaction plot the red line (BA-based PSAs) is not parallel with the other two, indicating an interaction. Applying the same analysis to the other two interaction plots reveals another interaction between soft monomer and CTA addition method and little interaction between CTA concentration and CTA addition method, in the range studied.

Figure 2 (right-hand side) also shows three response surface plots generated for $\ln(\text{shear})$. These represent a means to visually assess conditions producing the maximum $\ln(\text{shear})$. Examining the top surface plot, we see shear increases with decreasing CTA concentration and remains constant moving across the soft monomer axis; again indicating shear is independent of soft monomer type studied. The middle surface plot shows a saddle-like surface clearly indicating a region of maximum $\ln(\text{shear})$ with CTA addition method at 1.5, regardless of soft monomer type. Finally, the bottom surface plot shows highest $\ln(\text{shear})$ at the lowest CTA concentration and a region near CTA addition method 1.5.

The same trend analyses were performed for all the other response outputs (including results from rheological analysis), and a matrix summarizing main effects trends is shown as Table 3. This summary matrix lists a given variable's effect (positive or negative) as well as the strength of that effect (weak, moderate, or strong) on a given output as the variable moves from its lowest to highest level. The following bullet points summarize main effects trend observations for this DOE:

- Loop tack and peel adhesion (24 hour dwell) are dependent on soft monomer type while shear and peel adhesion (20 minute dwell) are independent of soft monomer type studied. A moderate negative effect on loop tack occurs with 2-EHA, while this parameter is indifferent to BA or the mixed monomer system. Conversely, a moderately positive effect is seen on peel (24 hour dwell) with the mixed monomer system while peel is not affected by either BA or 2-EHA. Rheology values of G' and G'' (at specific frequencies) all depend to some extent on soft monomer type, generally all showing a strong positive effect moving from 2-EHA to BA and strong negative effect switching from BA to mixed soft monomer.
- CTA concentration has a strong positive effect on loop tack and a strong negative effect on shear resistance (up to 0.25phm CTA). This suggests tack and shear cannot simultaneously be increased,

at least under conditions studied by this design of experiments. This is, in fact, a common difficulty in designing a PSA with well-balanced properties.

- The trend in CTA concentration for peel adhesion (both 20 minute and 24 hour dwells) is similar to that of loop tack, i.e., a strong positive effect is observed up to mid-level CTA concentrations, after which higher CTA levels decrease peel adhesion. This suggests optimal peel adhesion is obtained at medium CTA concentration. Changing CTA addition method from 1 to 2 has a strong negative effect on G' (10^2) and G'' (10^0), but little-to-no effect on G' (10^2) and G'' (10^2).

Table 3. Response Output Trend Summary Matrix.

| | Soft Monomer | [CTA] | CTA Addition Mode |
|---|---------------------------------------|---|---------------------------------|
| Loop Tack | ↔ (BA or BA/EHA) ++ ↓ effect (EHA) | +++ ↑ | +++ ↑ (1-1.5) + ↓ (>1.5) |
| 180° Peel (20') | ↔ | +++ ↑ (0.125-0.25) + ↓ to ↔ (>0.25) | + ↑ (1-1.5) +++ ↑ (1.5 to 2) |
| 180° Peel (24h) | ↔ (BA or EHA) ++ ↑ (BA/EHA) | +++ ↑ (0.125-0.375) +++ ↓ (0.375-0.5) | +++ ↑ (1-1.5) + ↓ (1.5-2) |
| Shear Resistance | ↔ | +++ ↓ (0.125-0.25) + ↓ (>0.375) | ↔ (1 - 1.5) +++ ↓ (at 2) |
| G' (10^2) | + ↑ (EHA-BA) + ↓ (BA-BA/EHA) | +++ ↓ (0.125-0.25) + ↑ (0.25-0.375) +++ ↓ (>0.375) | +++ ↓ |
| G' (10^0) | +++ ↑ (EHA-BA) +++ ↓ (BA-BA/EHA) | +++ ↓ (0.125-0.25) +++ ↑ (0.25-0.375) +++ ↓ (>0.375) | ++ ↓ |
| G' (10^2) | +++ ↑ (EHA-BA) +++ ↓ (BA-BA/EHA) | +++ ↓ (0.125-0.25) +++ ↑ (0.25-0.375) +++ ↓ (>0.375) | + ↓ to ↔ |
| G'' (10^2) | +++ ↑ (EHA-BA) +++ ↓ (BA-BA/EHA) | +++ ↓ (0.125-0.25) +++ ↑ (0.25-0.375) +++ ↓ (>0.375) | ↔ |
| tanδ (100) | +++ ↓ (EHA - BA) + ↑ (BA - BA/EHA) | ++ ↑ (0.125 - 0.25) ++ ↓ (0.25 - 0.375) ++ ↑ (>0.375) | ++ ↑ |

+, ++, +++ = weak, moderate, strong effect. Effect direction: ↑ increase, ↓ decrease, ↔ no effect.

PSA Response Surfaces

Empirical models were developed to quantify the strength of the main effects and interactions and to predict final PSA properties. Robust models were developed by removing insignificant first- and second-order terms ($\alpha = 0.05$) using backward regression procedure. Generally, the final models included only statistically significant terms (i.e., p-value < 0.05) although in certain cases non-significant terms had to be retained to preserve model hierarchy. Table 4 shows the models for all response outputs (FINAT test methods and rheology), except 180° peel adhesion (24 hour dwell), and their respective R^2 , R^2 -pred., and R^2 -adj., p-values for lack of fit and residuals. All models showed no lack of fit at $\alpha = 0.05$ (i.e., lack of fit p-value > 0.05) and residuals were normal and showed no trends.

Performance models with the highest R^2 -pred. values were ln(shear) (89.5%) and loop tack (72.7%), indicating an adequate ability to predict responses for new formulation levels. Furthermore, the R^2 -adj. values for these two models were high, with ln(shear)'s model adequately describing 94.8% of data variation and similarly 83.5% of data variation for loop tack. Peel adhesion was more difficult to model with 20 minute dwell peel adhesion having an R^2 -adj. of 65%. The R^2 -pred. value for this model was much lower than the previous two at 37.5%.

Rheology models were better than performance models in terms of correlation R^2 , R^2 -pred., and R^2 -adj. values; the R^2 -adj. values describing at least 85% of data variation. Additionally, G'' (10^2) and G' (10^2) models had the highest R^2 -pred. values of any model, both being greater than 92%. The other two rheological terms, G' (10^0) and G' (10^2), had lower correlation with R^2 -pred. values of 73.1% and 68.9%, respectively.

Table 4. Response Surface Regression Model Summary.

| Output | R ² | R ² -pred. | R ² -adj. | Lack-of-fit p-value | Residuals p-value | Model Equation |
|-----------------------|----------------|-----------------------|----------------------|---------------------|-------------------|---|
| In(Shear) | 97.0% | 89.5% | 94.8% | 0.188 | 0.330 | = B ₀ - B ₁ (SM)* - B ₂ (CTA) + B ₃ (CTA Add'n) + B ₄ (CTA) ² - B ₅ (CTA Add'n) ² + B ₆ (SM)(CTA Add'n) |
| Loop Tack | 91.8% | 72.7% | 83.5% | 0.790 | 0.350 | = B ₀ - B ₁ (SM)* - B ₂ (CTA) + B ₃ (CTA Add'n) + B ₄ (SM) ² - B ₅ (CTA Add'n) ² + B ₆ (SM)(CTA Add'n) + B ₇ (CTA)(CTA Add'n) |
| 180° Peel (20') | 75.0% | 37.5% | 65.0% | 0.132 | 0.504 | = B ₀ + B ₁ (CTA) - B ₂ (CTA Add'n) - B ₃ (CTA) ² + B ₄ (CTA Add'n) ² |
| G'(10 ²) | 91.8% | 68.9% | 85.6% | 14.35 | 0.693 | = B ₀ + B ₁ (SM)* - B ₂ (CTA) + B ₃ (CTA Add'n) - B ₄ (SM) ² + B ₅ (CTA) ² - B ₆ (CTA Add'n) ² |
| G'(10 ⁰) | 89.8% | 73.1% | 85.7% | 24.66 | 0.552 | = B ₀ + B ₁ (SM) - B ₂ (CTA) - B ₃ (CTA Add'n) - B ₄ (SM) ² |
| G'(10 ²) | 98.2% | 92.2% | 96.8% | 2.02E+08 | 0.123 | = B ₀ + B ₁ (SM) + B ₂ (CTA) + B ₃ (CTA Add'n) - B ₄ (SM) ² - B ₅ (SM)(CTA Add'n) - B ₆ (CTA)(CTA Add'n) |
| G''(10 ²) | 98.4% | 92.6% | 96.7% | 6.04E+07 | 0.430 | = B ₀ + B ₁ (SM) + B ₂ (CTA) + B ₃ (CTA Add'n)* - B ₄ (SM) ² - B ₅ (SM)(CTA) - B ₆ (SM)(CTA Add'n) - B ₇ (CTA)(CTA Add'n) |

* Denotes a term included to preserve model hierarchy, but is not significant.

In Table 4, the model coefficients have been rendered non-specific (B₀, B₁, B₂, etc.) for obvious reasons; however their direction of influence (negative or positive) is reported. The most important variable affecting ln(shear) was CTA concentration, both as a first-order and quadratic term, with the former having a negative influence and the latter a positive. Because both first and second-order CTA terms are influential indicates their relationship to ln(shear) is not strictly linear. The second most influential variable was CTA addition method, which had a moderately positive influence. These results are not unexpected considering that CTA level has a large impact on polymer molecular weight and cross-linking (gel fraction), traits directly effecting PSA cohesive strength (i.e., creep resistance). The negative (or inverse) influence stems from higher CTA concentrations producing lower molecular weight and gel fraction and therefore lower shear resistance. Soft monomer type was not found to be influential, i.e., shear resistance was independent of soft monomer; however a very minor synergistic effect (interaction) between soft monomer and CTA addition method was present. Not unexpectedly, the terms CTA and CTA² were also the most influential in the G' (10⁻²) model and followed the same direction, indicating good correlation between G' (10⁻²) and the time-scale for the onset of creep.

CTA concentration was the most influential variable for loop tack, with a strong negative influence, followed by a significant positive effect from the interaction of CTA concentration and CTA addition method. Similarly, the CTA concentration was also the most influential variable in the G' (10⁰) model, which corresponds to the bonding process in tack tests, and was again negative. The soft monomer was the second most influential factor for G' (10⁰). When considered alone, this inverse relationship of CTA concentration on both loop tack and G' (10⁰) is counter-intuitive. Tack might be expected to increase with CTA concentration, as (all else being equal) higher CTA concentration leads to lower molecular weight that can more easily wet out the substrate. However, the CTA concentration and CTA addition method interaction term, with its positive impact on loop tack, indicates that variables in addition to the CTA concentration play an influence. In addition, loop tack is also dependant on debonding frequency moduli, further complicating drawing conclusions based on a sole parameter.

In the 20 minute dwell peel adhesion model, while the quadratic term (CTA concentration)² and CTA concentration were the most influential, the correlation was poor (R²-pred. < 50%), therefore this model is not recommended. Further studies are needed to develop a better predictive approach for peel adhesion performance at 20 minute dwell. Finally, whereas CTA concentration dominated as the most influential variable for all other performance attributes, the soft monomer type was most influential in G' (10²) and G'' (10²). However, CTA concentration remained important as the second most influential factor.

In summary, the models clearly show CTA concentration was by far the most dominant variable, under the conditions studied with this experimental design. Future work will focus on validating these models through experimentation. For example, the model for shear will be used to calculate the variable levels to achieve a specific shear resistance (e.g., 1000 minutes) and a PSA will be made at those

formulation levels. Performance tests will then be performed to determine whether the shear resistance matches the predicted response.

Correlation of PSA Performance and Rheology

In order to develop models to predict shear resistance, loop tack and 180° peel adhesion from the linear viscoelastic behavior, namely G' and G'' moduli at specific frequencies, Minitab® 16 was used to plot performance metrics as response variables and frequency sweep data as predictor variables. Models were then based on fitted line regressions. For all plots, a linear regression model was found to be adequate for reflecting trends in the rheology data. Data normality and residual plots were examined for specific patterns and none were observed. Table 5 summarizes model regression equations, R^2 , and R^2 -adj. values as well as p-values for ANOVA and residuals ($\alpha = 0.05$).

The fitted line plot of $\ln(\text{shear})$ vs. $G' (10^{-2})$ shown in Figure 3 clearly shows a positive correlation between shear resistance and storage modulus at low frequencies. The correlation values of R^2 and R^2 -adj. are 63.9% and 61.2%, representing an adequate model describing 61% of the variation. Alternatively, an inverse correlation exists between loop tack and $\log(G' (10^0))$ (figure not shown, R^2 and R^2 -adj. of 61% and 58%, respectively). The increasing storage modulus indicates the PSA's higher resistance to flow, leading to low substrate wet-out, lower bonding efficiency and consequently lower loop tack. Plots for loop tack vs. $\log(G' (10^2))$ and $\log(G'' (10^2))$ are also inversely related, suggesting that lower moduli at the debonding frequency gives higher tack (R^2 -adj. approximately 50%). However, the data for loop tack vs. $\log(G' (10^2))$ was found to be non-normal, requiring additional model refinement.

Peel adhesion models were inadequate (R^2 and R^2 -adj. well below 50%). Recall that the response surface model for 20 minute dwell peel adhesion (Table 4) was not nearly as well correlated as those for $\ln(\text{shear})$ or loop tack, having R^2 -adj. and R^2 -pred. values of only 65% and 38%, respectively. The difficulty in developing satisfactory models for peel adhesion may lie in the high variability in the peel adhesion performance data itself, i.e., an inadequate measurement system. Therefore, attempts to correlate highly variable data with rheological behavior can only be expected to develop inadequate models. Chang² has demonstrated a good correlation between peel strength and rheological behavior. Consequently, it is expected rheology data is a better predictor of PSA performance than peel adhesion models.

Table 5. Performance Metrics vs. Rheology Linear Regression Model Summary.

| Output | R^2 | R^2 -adj. | ANOVA p-value | Residuals p-value | Model Equation |
|---|-------|-------------|---------------|-------------------|-----------------------------------|
| $\ln(\text{Shear})$ vs. $G' (10^{-2})$ | 63.9% | 61.2% | 0.000 | 0.140 | $y = 2.827 + 0.000169x$ |
| Loop Tack vs. $\log(G' (10^0))$ | 60.6% | 57.6% | 0.001 | 0.207 | $y = 37.26 - 6.26 \cdot \log(x)$ |
| Loop Tack vs. $\log(G' (10^2))$ | 59.2% | 56.0% | 0.001 | 0.020 | $y = 63.78 - 10.41 \cdot \log(x)$ |
| Loop Tack vs. $\log(G'' (10^2))$ | 53.2% | 49.6% | 0.002 | 0.192 | $y = 72.19 - 12.27 \cdot \log(x)$ |
| 180° Peel Adhesion (20') vs. $G' (10^{-2})$ | 51.7% | 48.0% | 0.003 | 0.025 | $y = 14.63 + 0.000358x$ |
| 180° Peel Adhesion (20') vs. $G' (10^2)$ | - | - | 0.112 | 0.059 | - |
| 180° Peel Adhesion (20') vs. $G'' (10^2)$ | - | - | 0.231 | 0.103 | - |
| 180° Peel Adhesion (24h) vs. $G' (10^{-2})$ | - | - | 0.095 | 0.473 | - |
| 180° Peel Adhesion (24h) vs. $G' (10^2)$ | - | - | 0.299 | 0.725 | - |
| 180° Peel Adhesion (24h) vs. $G'' (10^2)$ | - | - | 0.384 | 0.640 | - |

Conclusions

The effect of soft monomer type, CTA concentration and CTA addition method on a basic PSA's viscoelastic properties was studied. Both DOE analysis and empirical models indicate CTA concentration was the most influential variable for all response outputs. It had a strong positive effect on loop tack and a strong negative effect on shear resistance, indicating tack and shear cannot be simultaneously increased, at least under the studied conditions. In addition, mid-level CTA concentrations provided the highest peel adhesion.

In turn, through a Box-Behnken experimental design, the viscoelastic properties were related to conventional PSA test protocols. The best correlation was found between $\ln(\text{shear})$ and loop tack, indicating an adequate ability to predict adhesive performance as measured by standard test protocols (R^2 -pred. of 90% and 73%, respectively). Peel adhesion (20 minute dwell) proved more difficult to model (R^2 -pred. 38%), likely due to the variability in the peel adhesion test method itself. As a whole, the

adhesive's linear viscoelastic behavior as measured by G'' (10^2) and G' (10^2) proved the best correlation with the adhesive's performance (R^2 -pred. of $> 92\%$). In all cases, empirical models showed no lack of fit at $\alpha = 0.05$ and had normal residuals.

Fitted line regression plots were used to correlate performance metrics with rheological data and linear regression models were appropriate for all cases, based on the near zero ANOVA p-values. Adequate models were only found for correlating $\ln(\text{shear})$ with G' (10^{-2}) and loop tack with $\log(G' (10^0))$. The former model showed a positive correlation between shear and G' (10^{-2}). The latter model showed an inverse correlation between loop tack and $\log(G' (10^0))$ and described 58% of data variation. The negative correlation is expected, as the PSA becomes more rigid, indicated by the increasing storage modulus, it has a higher resistance to flow and substrate wet-out, which inevitably reduces bonding efficiency and thus loop tack. Models for loop tack and G' and G'' at debonding frequency were inadequate (R^2 -adj. approximately 50%). No adequate model was found for peel adhesion, likely due to the high variability in peel adhesion performance data, i.e., poor measurement systems.

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References

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2. E. P. Chang, *J. Adhesion*, 1997, **60**, 233-248.

Figure 1. G' and G'' vs. ω (rad/s) Plot for 2-EHA-based PSA Samples 1, 2, 9, and 11.

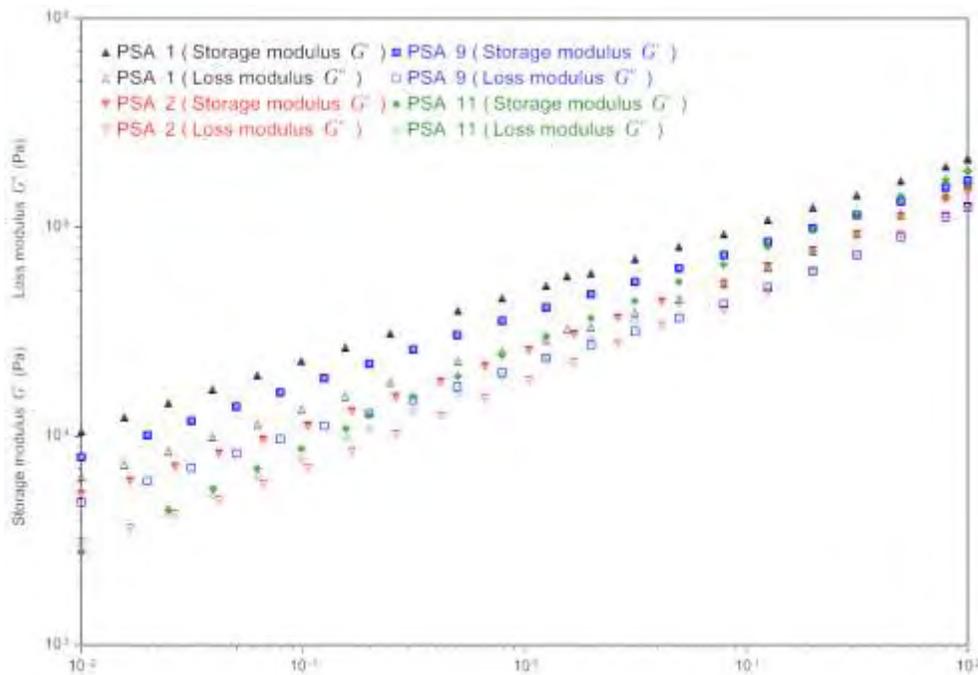


Figure 2. Main Effects, Interaction and Surface Plots for $\ln(\text{shear})$.

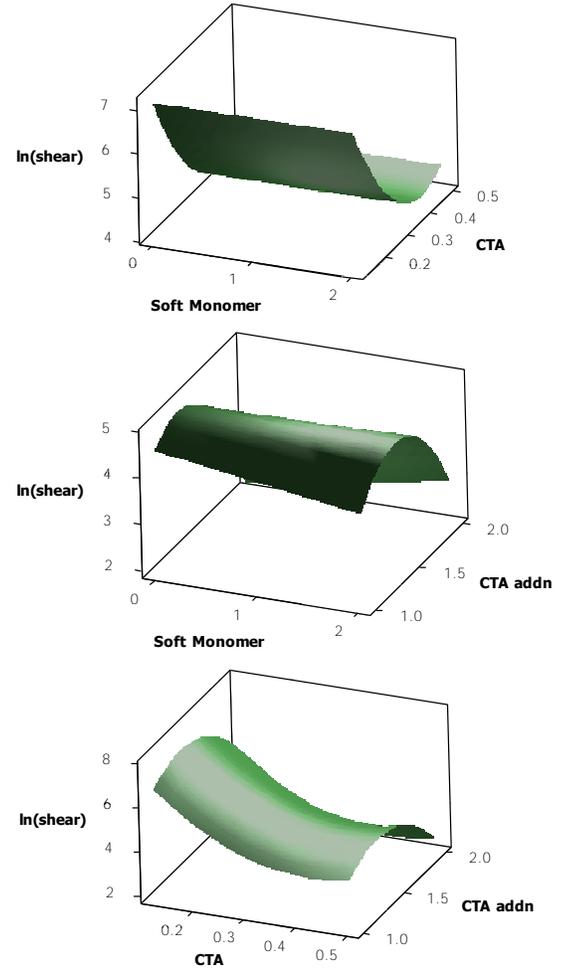
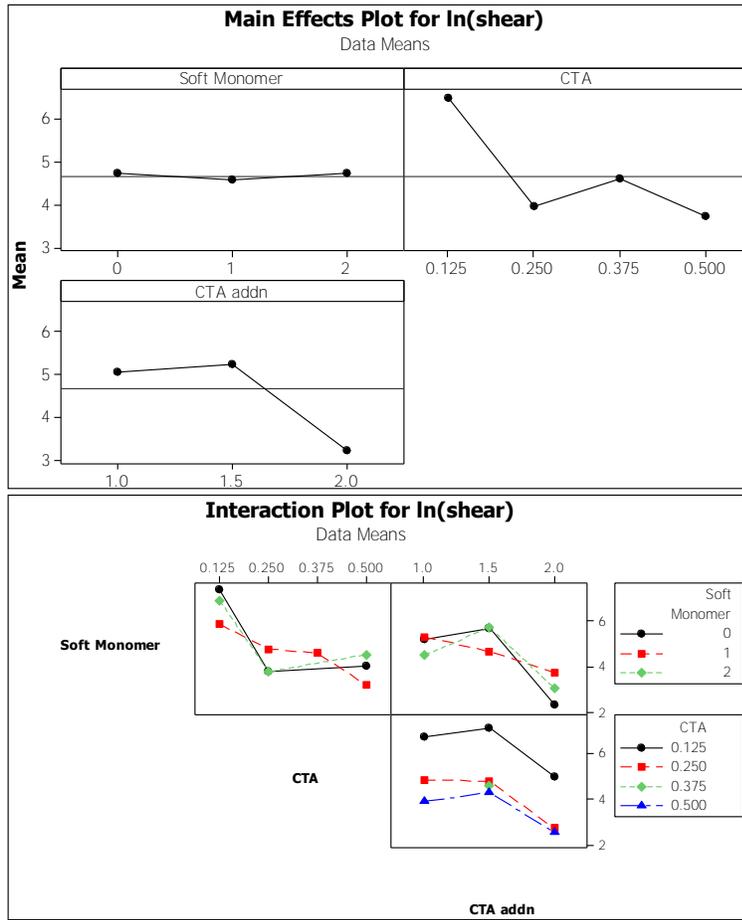


Figure 3. Fitted Line Plot for $\ln(\text{shear})$ vs. $G' (10^{-2})$.

