Accelerated Waterborne Pressure Sensitive Adhesive Development through Rheological Screening

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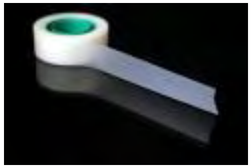
Agenda

- Waterborne Pressure Sensitive Adhesive Background
- Design of Experiment Approach
- Our Results
  - Trends
  - Models
  - Correlations
- Conclusions
- Newly developed WB PSAs

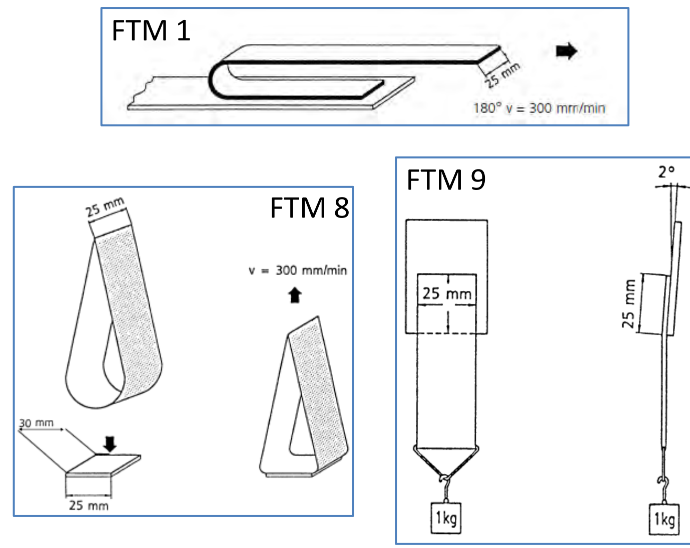


Pressure Sensitive Adhesives

- Adhesive materials which, when dry, possess a lasting & aggressive tack which enables them to adhere to a wide variety of substrates upon contact
  - Tapes & Labels

- PSA measured through 3 performance attributes
  - Tack: force required to remove from substrate
  - Peel: adhesive/substrate bond strength
  - Shear: cohesive strength

- Issues:
  - Time consuming
  - Film quality dependent
  - High variability



FINAT TECHNICAL HANDBOOK, Test Methods, 8th Edition, 2009

PSAs – Viscoelastic Materials

- Tack, Peel and Shear dependent on PSA bulk linear viscoelastic properties
  - Directly related to PSA response to imposed stress
  - Established correlation of deformation frequencies & adhesion test time-scales
    - $\omega = 10^{-2}$ to 10^{2} rad/s

- Rheology well known method for measuring PSA properties
  - Faster, more repeatable & representative of in-use performance
  - Screen & identify trends for synthetic parameters to achieve target properties

Adhesives Research

Our Goals:

- Investigate effects of PSA synthetic parameters on performance and viscoelastic properties
- Develop empirical models for predicting PSA performance
- Develop correlations between performance metrics & rheological behavior
- Utilize results to develop new WB PSAs

Experimental Design

- Box-Behnken Response Surface Design
  - Efficient estimation of 1st & 2nd-order coefficients
  - 3-factor, 3-level design with 2 replicates
- Generic WB PSA formulation
  - Fixed soft/hard M ratio
  - 400nm, 60% solids
  - Broad variable levels

– Soft Monomer type
– CTA concentration
– CTA addition method

- Evaluations (DOE outputs)
  - FINAT Test Methods
    - Loop Tack, 180^{o} Peel Adhesion & Shear resistance
      - Glass & Stainless Steel
  - Linear viscoelastic analysis using a rheometer

PSA #	Soft Monomer	[CTA]	CTA Addition Method
1	EHA	0.125	1.5
2	EHA	0.5	1.5
3	EHA/BA	0.125	1.5
4	EHA/BA	0.5	1.5
5	BA	0.125	1
6	BA	0.5	1
7	BA	0.125	2
8	BA	0.5	2
9	EHA	0.25	1
10	EHA/BA	0.25	1
11	EHA	0.25	2
12	EHA/BA	0.25	2
13	BA	0.25	1.5
14	BA	0.375	1.5
15	BA	0.375	1.5

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PSA Performance Results

PSA #	SM	P.S. nm	Dp_1[2] (vol%) nm	Dp_2[2] (vol%) nm	solids %	pH -	Tg °C
1	EHA	397	385	-	60.4	4.0	-41.9
2	EHA	410	411	-	60.8	4.0	-42.8
3	EHA/BA	227	391 (49)	61 (51)	60.4	4.4	-33.0
4	EHA/BA	230	400 (46)	74 (54)	60.8	4.5	-32.7
5	BA	253	381 (57)	72 (43)	60.4	4.1	-25.6
6	BA	260	383 (52)	103 (46)	60.3	3.9	-27.7
7	BA	240	383 (52)	70 (54)	60.2	4.0	-25.8
8	BA	279	476 (44)	99 (56)	61.0	4.1	-27.1
9	EHA	405	390	-	60.4	4.1	-38.9
10	EHA/BA	291	407 (63)	80 (37)	60.3	4.2	-31.5
11	EHA	399	385	-	60.7	4.3	-40.4
12	EHA/BA	436	429	-	60.2	4.2	-33.9
13	BA	434	423	-	60.3	4.0	-28.3
14	BA	439	435	-	60.2	4.3	-25.9
15	BA	434	426	-	60.1	4.0	-27.7

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

- Particle size within 10% of target
- Replicates agree well
- Wide T_g range: -42.8 to -25.6°C
- Bimodal particle size distribution with butyl acrylate

Achieved Latex Design Targets

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FINAT Test Method Results

PSA #	Loop Tack N	Peel (20') N/25mm	Peel (24h) N/25mm	Shear minutes
1	7.2 ± 0.9	8.0 ± 0.3	9.5 ± 0.5	1577 ± 390
2	11.1 ± 1.4	11.3 ± 0.3	17.7 ± 2.4[1]	56 ± 12
3	8.3 ± 1.4	7.8 ± 0.7	11.9 ± 1.6	1000 ± 124
4	10.3 ± 2.6	9.9 ± 0.6	21.4 ± 1.8[1]	93 ± 4
5	5.9 ± 2.4	5.5 ± 0.4	8.5 ± 0.5	841 ± 47
6	4.9 ± 3.1	11.1 ± 0.4	13.5 ± 0.4	48 ± 3
7	5.0 ± 1.2	9.6 ± 0.4	12.2 ± 1.0	147 ± 21
8	9.4 ± 1.3	12.6 ± 0.9[1]	9.7 ± 1.1[1]	13 ± 1
9	7.6 ± 2.1	9.6 ± 0.2	10.6 ± 0.3	179 ± 112
10	6.1 ± 2.1	8.2 ± 1.2	11.3 ± 0.5	90 ± 20
11	7.5 ± 2.5	15.8 ± 0.5[1]	16.1 ± 0.3[1]	11 ± 1
12	9.3 ± 2.5	20.0 ± 0.7[1]	20.2 ± 0.2[1]	21 ± 3
13	7.4 ± 1.6	9.9 ± 1.1	12.1 ± 0.1	119 ± 16
14	6.3 ± 1.1	10.6 ± 1.5	22.3 ± 4.2[1]	106 ± 2
15	7.7 ± 2.5	10.9 ± 1.7	16.4 ± 0.3[1]	93 ± 13

[1]Cohesive Failure, all others were clean plate.

- Distinct differences evident
- Wide performance range achieved
- Replicates agree within error

Achieved Significant Variation in Data

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Applying Rheology Correlation

- Based on Chang's Viscoelastic window concept
  - 10^{-2} to 10^{2} (rad/s) spans test time-scales
- Shear: low frequencies (creep)
  - $G'(10^{-2})$
- Peel and Tack: 2 process steps
  - Bonding favored by lower modulus at frequency
    - Peel $G'(10^{-2})$
    - Tack $G'(10^{0})$
  - Debonding
    - Cohesive strength: $G'(10^{2})$
    - Energy of dissipation: $G''(10^{2})$

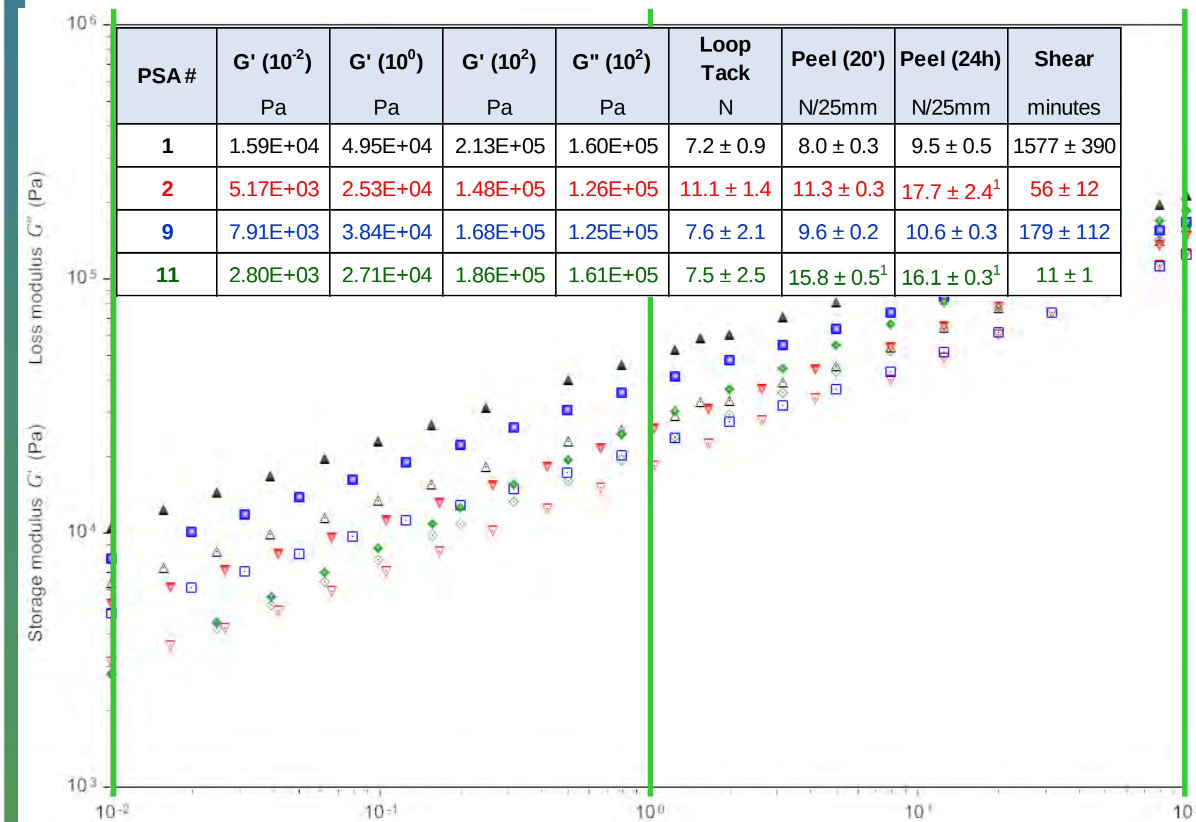
Shear
- High $G'(10^{-2})$

Peel
- Low $G'(10^{-2})$
- High $G'(10^{2})$
- High $G''(10^{2})$

Tack
- Low $G'(10^{-2})$
- High $G'(10^{2})$
- High $G''(10^{2})$

E.P. Chang, *J. Adhesion*, 1991, **34**, 189 -200, E.P. Chang, *J. Adhesion*, 1997, **60**, 233 -248

Results of Rheology Measurements



PSA #	G' (10^{-2}) Pa	G' (10^{0}) Pa	G' (10^{2}) Pa	G" (10^{2}) Pa	Loop Tack N	Peel (20') N/25mm	Peel (24h) N/25mm	Shear minutes
1	1.59E+04	4.95E+04	2.13E+05	1.60E+05	7.2 ± 0.9	8.0 ± 0.3	9.5 ± 0.5	1577 ± 390
2	5.17E+03	2.53E+04	1.48E+05	1.26E+05	11.1 ± 1.4	11.3 ± 0.3	17.7 ± 2.4[1]	56 ± 12
9	7.91E+03	3.84E+04	1.68E+05	1.25E+05	7.6 ± 2.1	9.6 ± 0.2	10.6 ± 0.3	179 ± 112
11	2.80E+03	2.71E+04	1.86E+05	1.61E+05	7.5 ± 2.5	15.8 ± 0.5[1]	16.1 ± 0.3[1]	11 ± 1

- G'(10^{-2}) trends correlate to shear data
- Tack & Peel more convoluted
- PSA2 had highest Tack
  - Lowest G'(10^{0})
  - But lowest G' & G"(10^{2})
- Bonding & debonding steps complicate Tack & Peel
  - Trends more difficult to discern

Rheology Can be Used to Discern Differences

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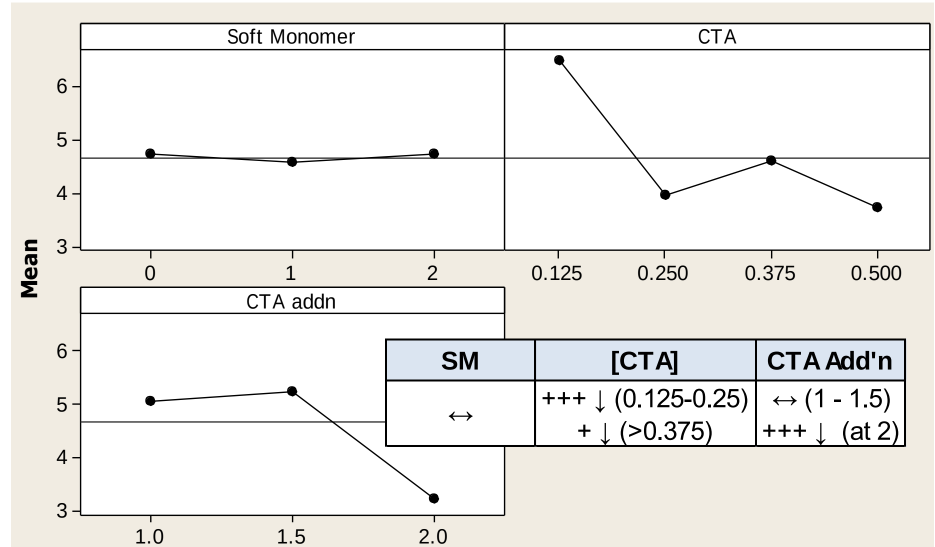
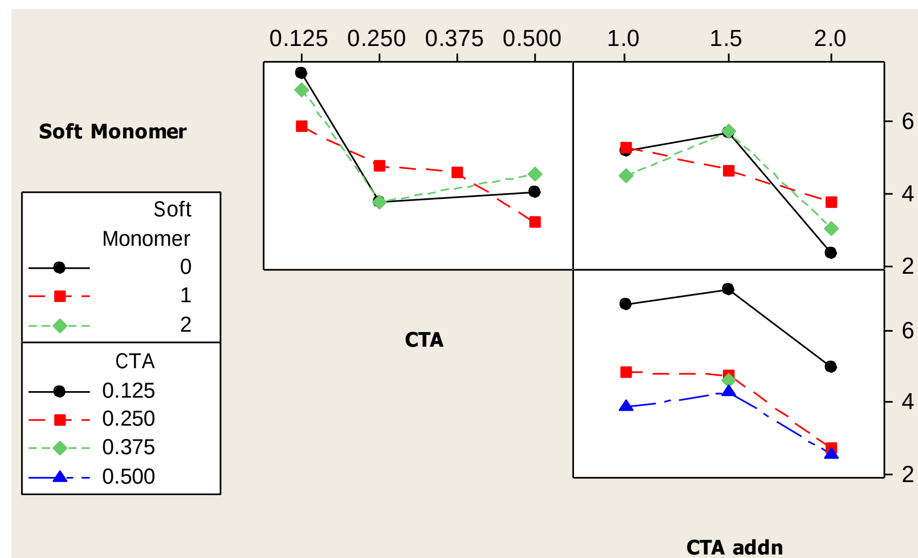
DOE Part 1: Trend Analysis

- Performance trend determination
  - Response surface regression analysis for 1st and 2nd order effects
- **Main Effects** - means plotted vs. each variable and each level (low to high)
  - Slope: effect strength & direction
- **Interactions** - means plotted vs. each variable at fixed level of 2nd variable
  - Parallel: no interaction
- SM interacts with CTA & CTA addition method
  - No interaction with CTA & CTA addition method



SM	[CTA]	CTA Add'n
↔	+++ ↓ (0.125-0.25) + ↓ (>0.375)	↔ (1 - 1.5) +++ ↓ (at 2)



Trend Analysis Summary Matrix

	Soft Monomer	[CTA]	CTA Addition Method
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)	↔

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

- Soft Monomer
  - Tack, Peel(24h), G′ and G″
  - No effect on Shear or P(20′)
- CTA concentration
  - Tack ↑ while Shear ↓
  - G′(10^{-2}) follows Shear's trend
  - Peel ↑ to a point
  - Optimal Peel at medium [CTA]
- CTA Addition Method
  - Effected Tack, Peel and Shear
  - 1 to 2 ↓ G′(10^{-2}) & (10^{0})

Trend Analysis Indicates [CTA] Most Influential Variable

DOE Part 2: Model Development

- Response surface models developed for tack, peel, shear and rheology metrics
  - Quantify strength of 1st and 2nd order effects
  - Predict PSA properties
- Model development methodology
  - Insignificant terms removed via backwards regression (α = 0.05)
  - Maximize correlation coefficients R^2, R^2-adj. and R^2-pred.

Output	R^2	R^2-pred.	R^2-adj.	Response Surface Model Equation
ln(Shear)	97.0%	89.5%	94.8%	$= B_0 - B_1(SM)^* - B_2(CTA) + B_3(CTA\ Add'n) + B_4(CTA)^2 - B_5(CTA\ Add'n)^2 + B_6(SM)(CTA\ Add'n)$
Loop Tack	91.8%	72.7%	83.5%	$= B_0 - B_1(SM)^* - B_2(CTA) + B_3(CTA\ Add'n) + B_4(SM)^2 - B_5(CTA\ Add'n)^2 + B_6(SM)(CTA\ Add'n) + B_7(CTA)(CTA\ Add'n)$
180^o Peel (20')	75.0%	37.5%	65.0%	$= B_0 + B1(CTA) - B2(CTA\ Add'n) - B_3(CTA)^2 + B_4(CTA\ Add'n)^2$
180^o Peel (24h)	61.0%	0.0%	39.3%	$= B_0 + B_1(CTA) + B_2(CTA\ Add'n)^* - B_3(CTA)^2 - B_4(CTA\ Add'n)^2 - B_5(CTA)(CTA\ Add'n)$
G'(10^{-2})	91.8%	68.9%	85.6%	$= B_0 + B_1(SM)^* - B_2(CTA) + B_3(CTA\ Add'n) - B_4(SM)^2 + B_5(CTA)^2 - B_6(CTA\ Add'n)^2$
G'(10^0)	89.8%	73.1%	85.7%	$= B_0 + B_1(SM) - B_2(CTA) - B_3(CTA\ Add'n) - B_4(SM)^2$
G'(10^2)	98.2%	92.2%	96.8%	$= B_0 +B_1(SM) + B_2(CTA) + B_3(CTA\ Add'n) - B_4(SM)^2 - B_5(SM)(CTA\ Add'n) - B_6(CTA)(CTA\ Add'n)$
G''(10^2)	98.4%	92.6%	96.7%	$= B_0 + B_1(SM) + B_2(CTA) + B_3(CTA\ Add'n)^* - B_4(SM)^2 - B_5(SM)(CTA) - B_6(SM)(CTA\ Add'n) - B_7(CTA)(CTA\ Add'n)$

* Denotes an insignificant term included to preserve model hierarchy.

Response Surface Model Predictability

Performance models

- Shear and tack: highest R^2-pred and R^{2-}adj.
  - Able to predict new responses and describe variation
- Peel proved more difficult to model

Rheological models

- Higher R^2-adj. than performance, described 85% of data variation
  - G' and G"(10^2) best predictors of all models
  - G'(10^0) and G'(10^{-2}) lower correlation

Output	R^2	R^2-pred.	R^2-adj.
ln(Shear)	97.0%	89.5%	94.8%
Loop Tack	91.8%	72.7%	83.5%
180° Peel (20')	75.0%	37.5%	65.0%
180° Peel (24h)	61.0%	0.0%	39.3%
G'(10^{-2})	91.8%	68.9%	85.6%
G'(10^0)	89.8%	73.1%	85.7%
G'(10^2)	98.2%	92.2%	96.8%
G''(10^2)	98.4%	92.6%	96.7%

Shear and Tack Models Able to Predict Performance

Response Surface Model Trends

Effect Strength (direction)	Strong	Medium
Shear Resistance	$(CTA)^2$ (+) & (CTA) (-)	(CTA Add'n) (+)
Loop Tack	(CTA) (-)	(CTA)(CTA Add'n) (+)
180^o Peel (20′)	$(CTA)^2$ (-)	(CTA) (+)
G′ (10^{-2})	$(CTA)^2$ (+) & (CTA) (-)	(CTA Add'n) (+)
G′ (10^0)	[CTA] (-)	SM (+)
G′ (10^2)	SM (+)	(CTA)(CTA Add'n) (-)
G″ (10^2)	SM (+)	(CTA)(CTA Add'n) (-)

- [CTA] known to effect molecular weight and gel fraction
  - Good correlation with G’(10^{-2}) and Shear
- Negative direction with Tack surprising
  - 2^{nd} order interaction term is positive

Models Indicate [CTA] Most Influential Variable

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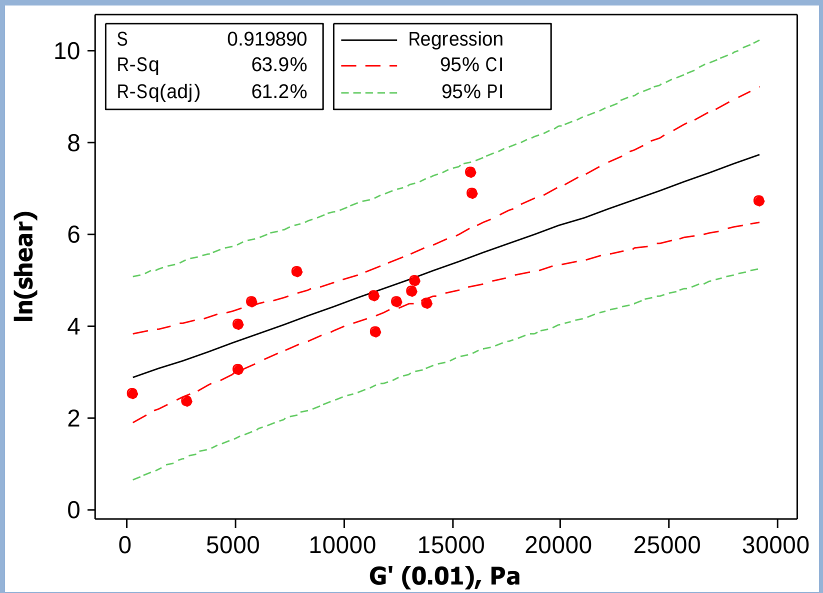
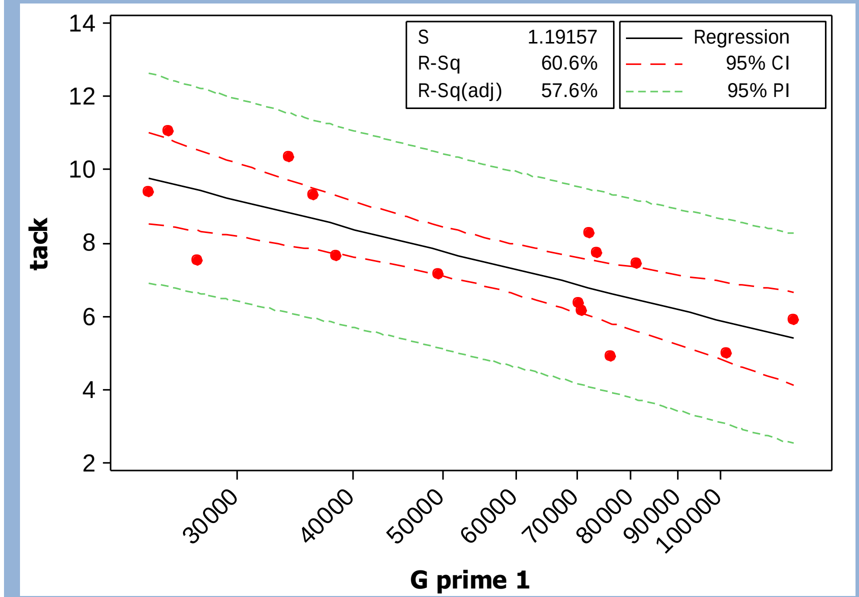
Correlation Models: Performance and Rheology

- FINAT metrics plotted vs. frequency data
- Models based on fitted line plot regressions
  - Linear regression models adequately reflected rheology data trends (low ANOVA values)



- Shear & G′(10^{-2}) – Positive correlation
- Adequate correlation values
- Model explains 61% of data variation



- Tack & G′(10^{0}) – Negative correlation
- Adequate correlation values
- As G′(10^{0}) ↑, higher flow resistance, lower wet-out and bonding efficiency = lower Tack

Correlation Models: Performance and Rheology

Output	R^2	R^2-adj.	ANOVA p-value	Residuals p-value	Model Equation
ln(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*log(x)
Loop Tack vs. log(G'(10^{2}))	59.2%	56.0%	0.001	0.020	y = 63.78 - 10.41*log(x)
Loop Tack vs. log(G"(10^{2}))	53.2%	49.6%	0.002	0.192	y = 72.19 - 12.27*log(x)
180^o Peel 20' vs. G'(10^{-2})	51.7%	48.0%	0.003	0.025	y = 14.63 + 0.000358x

- Negative correlation between tack versus log G′(10^2) and G″(10^2)
- Peel correlation models were inadequate
  - Recall, peel response surface models had lower correlations than tack and shear
  - Difficulty in developing adequate peel models may lie in high variability of peel adhesion data
- Chang demonstrated good correlation between peel and rheological behavior

Expect Rheology Data to be Better Predictor of PSA Performance than Peel Models

E.P. Chang, *J. Adhesion*, 1991, **34**, 189 -200, E.P. Chang, *J. Adhesion*, 1997, **60**, 233 -248

Conclusions

- CTA concentration was most influential variable for all responses in Box-Behnken experimental design
  - Strong positive effect on loop tack & strong negative effect on shear resistance
  - Peel adhesion highest at mid-level CTA concentrations
- Developed response surface models for both performance and rheological metrics
  - Shear and loop tack models had highest predictability (R2-pred.~90% & 73%)
  - Peel adhesion proved more difficult to model
- Correlation of FINAT metrics to rheological data resulted in adequate models for
  - shear to $G'(10^{-2})$ and loop tack to $\log(G'(10^{0}))$
- No adequate correlation model found for peel adhesion

DOE Analysis and Empirical Models Aligned

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Developed New Waterborne Adhesives

EPS® 150 – WB PSA

- **Filmic** label applications, including PVC film
  - APEO free
  - Acrylic-based
  - Good balance of tack, peel and shear
  - Very good water whitening resistance

Physical data		
Solids by weight	50% (± 1%)	ISO 3251
Viscosity at 23 °C (Brookfield, Spindle 2)	50 – 200 mPa.s	ISO 2555
pH value	4.0 – 6.0	ISO 976

Typical values		
Density at 20 °C	approx. 1055 kg/m^3	
Freeze/thaw stability	not resistant	
Tg	approx. -30 °C	
Shear adhesion	80 hr	1 in^2/1.8kg*
Loop tack	14 N	FINAT 9*
Peel 20 min.	10 N	FINAT 1*
Peel 24 hour	11 N	FINAT 1*

* Coated 15 g/m^2 on 36 µm polyester film, adhesion to glass.

EPS® 157M – WB Coater Ready PSA

- **General purpose** label applications
  - APEO free
  - Acrylic-based
  - Good balance of tack, peel and shear

Physical data		
Solids by weight	57% (± 1%)	ISO 3251
Viscosity at 23 °C (Brookfield, Spindle 2)	180 – 250 mPa.s	ISO 2555
pH value	7.0 – 8.5	ISO 976

Typical values		
Density at 20 °C	approx. 1055 kg/m^3	
Freeze/thaw stability	not resistant	
Tg	approx. -40 °C	

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Thank You!

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