FORMULATING UV-CURABLE ACRYLIC PRESSURE SENSITIVE ADHESIVES FOR THE ARCHITECTURAL CONSTRUCTION INDUSTRY

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1. Introduction

Peel and stick pressure sensitive adhesive (PSA) products are well suited for the building industry¹. Specifically, UV-Curable hot melt acrylic PSAs are attractive due to their broad range of installation and service temperatures, excellent moisture resistance, the ability to deposit high coat weights (> 5 mil), and solvent free chemistry. These adhesives offer superior green tack in cold environments (T < 32 °F) due to their low glass transition temperature, but also retain shear performance at high temperatures (T > 140 °F) due to the presence of chemically crosslinked networks. To expand the range of applications, UV-curable acrylic hot melts can be formulated with additives such as tackifiers and acrylic block copolymers. In this paper, we describe several formulating strategies for UV-cure acrylic hot melt adhesives to target specific performance attributes.

2. Methods

To explore the independent and interacting effects of composition and cure dosage on PSA performance, a Box-Behnken experimental design² was employed using the compositions listed in **Table 1**. A UV-curable acrylic hot melt resin (here forth referred to as "acrylic resin") with an uncured T_g of -39 °C was the primary component in all formulations used for this study. The additives used for formulation included a nonfunctionalized MMA-BA-MMA block copolymer with approximately 20% MMA content (here forth referred to as "copolymer"), and a fully hydrogenated rosin ester tackifier with a softening point of 85 °C. All raw materials are commercially available. The experimental design explored three factors (copolymer content, tackifier content, and UV cure dose) and three responses (180° peel force, loop tack force, and static shear failure time).

In addition to the compositions listed in **Table 1**, the samples shown in **Table 2** were also included in the study to expand the compositional space of interest and to provide an unformulated acrylic resin reference point. A ternary diagram illustrating the composition space of explored in this study is shown in **Figure 1**.

Sample:	С	D	Е	F	G	Н	Ι	J
Acrylic Resin (%	81.0	81.0	76.0	76.0	81.5	81.5	75.5	75.5
wt.)								
Copolymer (% wt.)	10.0	10.0	15.0	15.0	12.5	12.5	12.5	12.5
Tackifier (% wt.)	9.0	9.0	9.0	9.0	6.0	6.0	12.0	12.0
Cure Dose (mJ/cm ²)	75.0	150.0	75.0	150.0	75.0	150.0	75.0	150.0
Coat Weight (g/m ²)	173.4	173.4	191.0	191.0	187.5	187.5	172.9	172.9
Sample:	Κ	L	М	Ν	Р			
Acrylic Resin (%	84.0	79.0	78.0	73.0	78.5			
wt.)								
Copolymer (% wt.)	10.0	15.0	10.0	15.0	12.5			
Tackifier (% wt.)	6.0	6.0	12.0	12.0	9.0			
Cure Dose (mJ/cm ²)	112.5	112.5	112.5	112.5	112.5			
Coat Weight (g/m ²)	172.4	168.7	161.3	171.0	173.2			

Table 1. Compositions used for Box-Behnken experimental design.

 Table 2. Additional compositions included in this study.

Samp	ole: A	В	S	Т	U	V
Acrylic Resin	(% 100	100	80.0	80.0	90.0	90.0
wt.)						
Copolymer (% wt.)) –	-	20.0	20.0	-	-
Tackifier (% wt.)	-	-	-	-	10.0	10.0
Cure Dose (mJ/cm ²	²) 75.0	150.0	75.0	150.0	75.0	150.0
Coat weight (g/m ²)	170.7	170.7	168.2	168.2	173.4	173.4



Figure 1. Ternary diagram illustrating composition space explored in this study.

Formulations were prepared by first heating pure copolymer to approximately 180 °C with slow agitation using a heating mantle and paddle mixer to obtain a homogenized copolymer melt. While maintaining agitation, the copolymer melt was cooled to 120 - 130 °C before adding molten (120 °C) acrylic resin in a slow stepwise manner to avoid formation of localized cold spots during blending. Once the blend was homogenized, it was cooled to 100 °C, while maintaining agitation before adding room temperature tackifier pellets. Homogenized formulations were cooled to room temperature for storage prior to use.

Coating was conducted on a custom coating table utilizing a heated vacuum table and adjustable height Byrd bar. Formulations were melted immediately prior to coating and direct coated onto 2 mil chemically treated PET film using a table temperature of approximately 210 °C (samples A and B used a table temperature of approximately 150 °C). Coating weights were determined by the mass difference method and are listed in **Table 1** and **Table 2**. Coated sheets were cured using a single pass through a UV curing station. The UV exposure was confirmed at the time of curing using an in-line UV exposure meter. Cured sheets were then cooled, hand roll laminated to 40# siliconized paper release liner, and conditioned at 73 °F and 50% relative humidity (i.e. "controlled temperature and humidity" or "CTH") for at least 24 hours prior to preparing test strips.

All PSA tests were conducted at CTH on stainless steel panels. Strips were cut to 1" wide and rolled down on cleaned stainless steel panels using test procedures consistent with PSTC test methods. Roll downs were conducted using a roll down machine operating with 4.5 lbs weighted rollers using one forward and one reverse pass at a speed of 12 in/min. Peel testing was conducted for both 30 minute and 24 hour on-panel dwell times and employed a 180° pull geometry at a pull rate of 12 in/min. Each PSA measurement was conducted in replicates of five strips, unless otherwise noted. Static shear testing was conducted with a 1 inch x 2 inch overlap and 0.500 kg weight, unless otherwise noted. Loop tack testing was conducted on a standard loop tack instrument using 1 inch wide strips. On rare occasions, data points exceeding 2 standard deviations from the average value were considered outliers and were removed.

Select samples of coated sheets were also analyzed via atomic force microscopy (AFM) to obtain height and phase maps. AFM samples were prepared by affixing coated constructions to AFM sample pucks and peeling away release liner to expose the adhesive immediately prior to imaging. Imaging was conducted at room temperature using super sharp silicon probes with a spring constant of 10-30 N/m, operated at a low imaging setpoint and high drive amplitudes. Super sharp tips (< 5 nm radius) were used to minimize surface contact with the adhesive films and permit imaging of low-T_g particles at the adhesive surface with minimal sample distortion.

3. Results and Discussion

The separate effects of tackifier and copolymer were investigated using the formulations shown in **Table 2**. The AFM images shown in **Figure 2** and

Figure 3 confirm that the tackifier is completely miscible in the acrylic resin, as expected.

The copolymer additive is markedly less miscible in the acrylic resin compared to tackifier, favoring the formation of dispersed particles, as shown in **Figure 4**. The particles appear to be uniform in size (\sim 100 nm) and spacing (100 - 200 nm). In addition, the particles consist of a core shell structure, in which a lower elastic modulus shell surrounds a higher elastic modulus core. In

Figure 5, semicrystalline lamellar domains of poorly dispersed copolymer can also be seen. It is hypothesized that these lamellar structures, and the core shell architecture of the dispersed copolymer particles, are due to phase separation of the copolymer block segments due to differing degrees of hardness and polarity between the MMA and BA block segments. The shells of the particles are expected to be BA rich, due to favorable interactions with the BA based acrylic resin.



Figure 2. AFM images of pure acrylic resin representing spatial maps of height (A, C) and phase (B, D).



Figure 3. AFM images of height (A, C) and phase (B, D) for sample V showing excellent miscibility of tackifier in the acrylic resin.



Figure 4. AFM images of height (A, C, E) and phase (B, D, F) for sample T showing phase separation of copolymer additive in acrylic resin. Particles exhibit a core shell morphology.



Figure 5. AFM images of height (A, C) and phase (B, D) for sample T showing a region of poorly dispersed semicrystalline copolymer.

The data in **Figure 6** illustrate the independent effects of copolymer content, tackifier content, and cure dosage on peel performance after 30 minutes on panel. Neat acrylic resin exhibits a negligible change in peel performance with increased cure dosage, suggesting that the cure depth is slightly less than the full thickness of the adhesive, due to strong UV-C absorption by the crosslinker photoinitiator content.

The introduction of copolymer results in a slight reduction in peel performance compared to neat acrylic resin. Although this behavior is certainly related to the presence of relatively hard, high melting point copolymer particles at the adhesive surface impeding wet out and anchorage of the acrylic resin, the behavior can also be explained by a difference in cure efficiency. Copolymer blends exhibit systematically lower peel performance (approximately 20% lower) than neat acrylic resin samples, suggesting more cross linking may be occurring in these films compared to neat acrylic resin samples prepared with identical cure dosage and coat weights. This is likely due to a deeper depth of cure in coatings containing copolymer, due to a combination of 20% less acrylic resin content and enhanced internal scattering of UV-C light through the copolymer particles (which are comparable in size to UV-C wavelengths). The change in failure mode from cohesive failure at 75 mJ/cm² (sample S) to adhesive failure at 150 mJ/cm² (Sample T) also supports this hypothesis. The larger variation in peel values for copolymer samples is likely due to the presence of larger, poorly dispersed domains of copolymer like those observed in **Figure 5**.

The effect of tackifier content is significantly stronger than that of copolymer content. As expected, the introduction of tackifier reduces both peel and shear performance relative to the neat acrylic resin due to the softening effect of the rosin ester. **Figure 7** shows that increasing cure dosage results in marginal recovery of shear performance for the tackified formulation, however the tackified formulations remain significantly lower in shear performance than the neat acrylic resin samples and copolymer blends, as

expected. This data suggests formulations U and V are over-tackified due to the significant drop in PSA performance relative to neat acrylic resin.



Figure 6. Peel performance of samples A, B, S, T, U, and V. Peel data was collected after 30 minutes on panel dwell time.



Figure 7. Static shear collected for samples A, B, S, T, U, and V after 30 minutes on panel dwell time. Note the strong influence of tackifier and cure dosage for samples U and V.

To further examine the effect of copolymer content, tackifier content, and cure dosage, and to identify interacting effects of these factors, the compositions shown in **Table 1** were evaluated as an experimental design and augmented with select AFM measurements. **Figure 8** and **Figure 9** show AFM height and phase maps for Samples D and F, respectively. Both samples contain copolymer and tackifier, but in differing amounts, and exhibit similar morphologies to that shown for Sample T in **Figure 4**. This suggests interacting effects between the tackifier and copolymer are likely to be weak, due to poor phase interaction between these two additives.

The copolymer particle sizes (~100 nm) and shell thickness appear to be independent of copolymer content in the range of 10 - 20% loading, as seen by comparing **Figure 4**, **Figure 8**, and **Figure 9**. Particles are, however, more difficult to resolve in **Figure 8** due to the comparable contents of tackifier

and copolymer. It is unclear if this behavior is simply due to a softer matrix that is more difficult to image in high resolution, or if the introduction of tackifier also improves the miscibility of copolymer with acrylic resin.

Despite negligible differences in morphology between the sample blends, significant differences in PSA performance were observed. Using quadratic least squares regression, the PSA results from the formulations shown in **Table 1**, were empirically modeled.

Static shear data was fit to the model shown in **Equation 1** and **Table 3**, and corresponding contour plots for high, middle, and low factor levels are shown in **Figure 10**. Due to the high coat weight employed in this study, static shear performance is considered generally low, but statistically significant trends were still observable (see **Figure 15** in the Appendix). Tackifier content, copolymer content, and cure dosage were significant factors, as expected. Cure dosage exhibited both a strong quadratic effect and pairwise interactions with the tackifier and copolymer. Pairwise interactions between the tackifier and copolymer directly were not significant, which is consistent with the AFM observations already discussed.



Figure 8. AFM images of height (A, C) and phase (B, D) for sample D.



Figure 9. AFM images of height (A, C) and phase (B, D) for sample F.

Table 3. Statistical parameters for the static shear model fit listed in order of decreasing significance (*P-Value*). The values of corresponding fit constants (C_i) for each model term are also shown, along with adjusted R-squared (R^2_{adj}) and prediction R-squared (R^2_{pred}) values.

Term	C_i	P-Value
Constant	471.3	0.000
Tackifier	-320.1	0.000
Cure Dose	193.6	0.000
Cure Dose * Tackifier	-161.6	0.000
(Tackifier) ²	137.5	0.000
Copolymer	109.5	0.000
Cure Dose * Copolymer	87.8	0.001
$(Cure Dose)^2$	99.5	0.002
P Value < 0.050 are significant for 0.5% confidence interval		

P-Value < 0.050 are significant for 95% confidence interval

\mathbf{R}^{2}_{adj} :	88.88 %
R^2_{pred} :	86.70 %

$$f_{shear} = C_0 + C_1 T + C_2 E + C_3 P + C_4 T^2 + C_5 E^2 + C_6 T E + C_7 P E$$

Equation 1



Figure 10. Contour plots for static shear results on samples shown in Table 1. Black dots indicate measurement points.

Specific trends for static shear performance are observed in **Figure 10**. In general, cure dosage and copolymer content improve shear performance, and tackifier content reduces shear performance, as expected. Cure dosage exhibits the strongest effect, particularly at low tackifier levels. At tackifier content greater than ~10%, the effects of copolymer and cure dosage are strongly suppressed, due to an excess of cold flow behavior and reduced UV-C penetration depth at high tackifier loadings.

Peel performance was evaluated in a similar manner. The model for peel testing (measured after 24 hrs on panel, here forth referred to as "24 hr peel") is detailed in **Table 4** and **Equation 2**, with corresponding contour plots shown in **Figure 11**. Data for the 24 hr peel test exhibits a significant dependence on cure dose and tackifier content. Interestingly, a pairwise interaction between tackifier and copolymer content was also found to be significant. In addition to these factors, the 24 hr peel model is also sensitive to a pairwise interaction between tackifier and cure dose, as well as quadratic dependencies on cure dose and tackifier content. Although copolymer content was considered insignificant (for a 95% confidence interval), this factor was retained to maintain a hierarchical model structure, and to reflect prior knowledge that copolymer content is known to affect peel performance.

Table 4. Statistical parameters for the 24 hr peel model fit listed in order of decreasing significance (*P*-*Value*). The values of corresponding fit constants (C_i) for each model term are also shown, along with adjusted R-squared (R^2_{adj}) and prediction R-squared (R^2_{pred}) values.

Term	C_i	P-Value
Constant	6.657	0.000
Cure Dose	0.748	0.000
Tackifier	-0.654	0.000
Tackifier * Copolymer	0.386	0.000
Tackifier * Cure Dose	-0.366	0.001
$(Cure Dose)^2$	0.367	0.005
(Tackifier) ²	0.260	0.041
Copolymer	0.024	0.745

P-Value < 0.050 are significant for 95% confidence interval

R^2_{adj} :	76.76 %
R^{2}_{pred} :	73.06 %

 $f_{24 hr peel} = C_0 + C_1 T + C_2 E + C_3 P + C_4 E^2 + C_5 T^2 + C_6 T E + C_7 T P$

Equation 2



Figure 11. Contour plots for 24 hr peel results on samples shown in Table 1. Black dots indicate measurement points.

Several interesting trends are observed in **Figure 11**. As expected, peel performance generally increases with increasing cure dosage and decreasing tackifier content. At very high tackifier content, the effect of cure dose is suppressed, due to reduced cross linking density caused by dilution effect of tackifier on the acrylic resin.

Although tackifier and copolymer effects are suppressed for samples prepared with low cure dosages (due to a generally low degree of crosslinking), the dependence of peel performance on copolymer content is more complex at cure dosages above 112 mJ/cm². For these higher cure dosages, copolymer content dampens the effect of tackifier for 24 hr peel. This is likely due to two contributing causes: (1) a higher copolymer content impeding the cold flow migration of tackifier, resulting in improved anchorage, and (2) the abundance of soft shell copolymer particles near the substrate interface promoting localized tack and anchorage. Expanding further on cause (2), it can be seen from **Figure 4**(F) that the copolymer particle shells exhibit an elastic modulus softer than that of the surrounding acrylic resin matrix. Therefore, it is reasonable to assume that the shells of these particles likely offer locally enhanced tack and anchorage compared to the surrounding acrylic resin, and a higher concentration of particles should provide some improvement of tack and anchorage.

Table 5. Statistical parameters for the loop tack model fit listed in order of decreasing significance (*P*-*Value*). The values of corresponding fit constants (C_i) for each model term are also shown, along with adjusted R-squared (R^2_{adj}) and prediction R-squared (R^2_{pred}) values.

Term	C_i	P-Value
Constant	6.868	0.000
Tackifier	0.668	0.000
Copolymer	-0.593	0.000
Cure Dose	-0.383	0.003
Tackifier * Copolymer	-0.383	0.030

P-Value < 0.050 are significant for 95% confidence interval

R^{2}_{adj} :	50.10 %
R^{2}_{pred} :	45.99 %

$$f_{tack} = C_0 + C_1 T + C_2 E + C_3 P + C_4 P T$$

Equation 3



Figure 12. Contour plots for loop tack results on samples shown in Table 1. Black dots indicate measurement points.

The fitted model for loop tack is detailed in **Table 5** and **Equation 3** with corresponding contour plots shown in **Figure 12**. The precision of the loop tack model is considerably worse than the peel and shear models due to poor statistical differentiation between most sample measurements, as shown in **Figure 14** in the Appendix. Therefore, the contour plot curvatures and choice of significant terms should be interpreted with caution. Nevertheless, useful information can still be obtained from this analysis.

The model suggests that tackifier, copolymer, and cure dose are all significant factors, with tackifier content dominating the model behavior, as expected. A weak pairwise interaction between tackifier and copolymer is also present.

The trends observed in the contour plots of **Figure 12** are also consistent with expectations. Generally, increasing tackifier content improves tack performance, while increasing cure dosage and copolymer content reduce tack performance. These effects appear to be largely independent, but they are strongly suppressed in high copolymer or low tackifier compositions.

4. Conclusion

The use of block copolymer and tackifier additives to customize the peel, shear, and tack performance of UV-curable acrylic hot melt adhesives has been demonstrated at coat weights of interest to the architectural construction industry. This formulation approach can be utilized as an additional tuning method to achieve desirable PSA performance in addition to, or instead of, the standard approach of modulating UV curing exposure and coat weight. Specifically, the introduction of a block copolymer has been shown to offer better repositionability (i.e. lower initial tack) without compromising peel and shear performance. Copolymer has also been demonstrated as a useful additive to amplify the effect of cure dosage at improving shear performance. By extending this formulation approach, UV-curable acrylic hot melt adhesives can be tailored to address unique adhesion challenges in a variety of new applications.

5. Appendix



Figure 13. Peel data for samples shown in Table 1 showing standard deviations of replicate measurements, relative performance compared to neat acrylic resin samples A and B, and the close agreement between 30 minutes on panel and 24 minutes on panel at controlled temperature and humidity (CTH) contitions.



Figure 14. Loop tack data for samples shown in **Table 1** showing standard deviations of replicate measurements and relative performance compared to neat acrylic resin samples A and B. Note the lack of stastitical differentiation among most samples.



Figure 15. Static shear data for samples shown in Table 1 showing standard deviations of replicate measurements and relative performance compared to neat acrylic resin samples A and B.

6. Acknowledgements

The authors would like to acknowledge Kyle Dayak, Nora Gjokaj, and Jerome Jourdan for their contributions to experiments and analysis, as well as Sujith Chacko, David Tappa, and Ying Jing for their assistance with coordinating technical resources.

7. Literature Citations

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