REMOVABLE WATER-BASED ADHESIVE TECHNOLOGY FOR GRAPHICS APPLICATIONS

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Introduction

Water-based pressure sensitive adhesives (PSAs) are a growing market due in part to the ease of use, high solids content, good conversion rates and speed of coating, but obstacles still stand in its way when competing with other technologies. While solvent-based systems often boast higher performance, growing environmental concerns have given rise to increasing popularity of water-based systems. Additionally, as customer demand for differentiated products grows, finding solutions to application needs will continue to become more complex. In order to bridge the gap between these technologies and application challenges, a fundamental review of water-based removable technology and a discussion on design parameters will follow. Topics reviewed will include the importance of the design factors of surfactant systems, monomer composition, crosslinking technologies, and molecular weight control. The impact of these properties on key performance metrics, such as adhesion level, anchorage, and long-term removability will be demonstrated as well. Franklin's holistic approach of combining these design factors has shown a positive change in the key application parameters of long-term, clean removability of the adhesive.

Structure-Property Relationships Overview

Polymer systems are a complicated interconnection of many physical and chemical properties. In order to better understand the impact of various changes, these properties are often broken down into multiple sub-categories. In the following review, several categories are explored in more detail to illuminate the cause and effect of the response on the final performance of the adhesive. Key categories include the use of surfactants, monomer composition, molecular weight control, and crosslinkers.

Surfactants

Surfactant selection is a key component of any water-based emulsion. The surfactants chosen often serve multiple functions. Primarily, surfactants act as stabilizing ingredients to maintain the inherent high energy state of an emulsion. Improper selection of surfactants will allow latex coagulation to occur more readily. Long-term shelf-life studies can be done to probe the overall stability of a latex to assist in determining the proper choice of surfactant. These primary stabilizing agents will also influence the particle size of the final emulsion. Secondly, surfactants are used to lower surface tension of an emulsion. Water-borne emulsions must be used in the field on coating operations that often require a low surface energy release coat to carry the adhesive. This process, typically called transfer coating, allows manufacturers to dry the emulsion without damaging the final facestock. Therefore, it is imperative the emulsion can withstand the harsh shearing force of the operation while simultaneously maintaining low surface tension to readily wet low surface energy substrates.

With this in mind, let’s look at particle size control. Surfactants, when added into a bulk tank of water, will begin to form micelles. Each surfactant has a critical micelle concentration, or CMC, specific to that surfactant. By varying the amount and type of surfactant, micelle formation can be controlled. These micelles are the catalyst for particle formation, thereby allowing those trained in the art to control the particle number of the final latex. Other parameters can be used to further manipulate particle nucleation, but for the examples below only the surfactant has been varied. The third example is shown with a reduction in solids content.

Table 1. Particle Size and Viscosity as a Function of Surfactant and Solids

Polymer	**Theoretical Solids [%]**	**Particle Size [nm]**	**Viscosity [cP]**	**Grit [ppm]**
Surfactant A	60	382	110	10
Surfactant B	60	180	8240	16
Surfactant B	55	166	126	9

As shown in **Table 1** above, the surfactant used in building the polymer system can have a large impact on the final latex. When a system is made using Surfactant A, the resulting particle size is much larger than the same system made with Surfactant B. These differences arise from the number of particles nucleated during the polymerization process. Since Surfactant B is able to stabilize particles with less surface coverage, this leads to more particles, assuming the same amount of total surfactant is used. Each polymer used the same amount of monomer in the feeds; therefore, the monomer will spread out to more particles, resulting in the smaller final particle size. This simple example illustrates the ease with which surfactants can manipulate latex particles. As noted in the table, the viscosity has risen dramatically as a result of the switch from Surfactant A to Surfactant B. As particle size decreases, the surface area of the particles increases. This leads to more surface area between particles available to interact with each other, often resulting in a higher viscosity. A viscosity this high will likely face problems in a manufacturing environment, but if the smaller particle size is desirable for other reasons, a method to maintain low viscosity is needed. The third entry in the table showcases this; by decreasing the theoretical solids of the product, the small particle size can be accommodated without a ruinous increase in viscosity.

Changing the type of surfactant will also impact the performance. Nonionic and anionic surfactants are most commonly used and are the focus of these studies, but cationic and amphoteric surfactants have usage as well. For stabilizing polymer particles, typically anionic surfactants contribute to electrostatics, nonionic surfactants contribute to steric stabilization [2]. These differences can be used to modify unstable products. Furthermore, anionic surfactants often impact particle nucleation more strongly; nonionic surfactants typically improve storage stability. Surfactants must stabilize the final latex for extended periods of time, so close consideration must be given in their selection. To complicate matters, the particle size must also be considered when evaluating storage stability. In the following table, two polymers with different particle sizes are shown.

Table 2. Particle Size Impact on Shelf Stability

Polymer Characteristics		Initial Results		6 Month Accelerated Aging Results		
Polymer Process	**Particle Size [nm]**	**Viscosity [cP]**	**Solids [%]**	**Viscosity [cP]**	**Solids [%]**	**Observations**
Seeded	210	174	60.3	108	48.5	Settling
Unseeded	440	88	60.5	84	60.6	Stable

For both polymers, the same ingredients were used, but the process differed. The first polymer was seeded whereas the second polymer was not. Seeding a polymer batch can be done in several ways. In this example, a small amount of surfactant and monomer were allowed to react before polymerization feeds began. The unseeded batch simply began polymerization feeds without the initial reaction. By controlling the reaction in this manner, different particle sizes with the same ingredients can be made. It is also important to note the impact on surface area as particle size decreases. These properties are inversely proportional, meaning more surface area results in decreased particle size. Both processes yielded a product that was initially stable and similar in both solids and viscosity; however, upon accelerated aging in a 70ºC oven, the contrast between the two was clear. The seeded, smaller particle latex exhibited significant settling, dropping in solids content drastically due to coagulum forming at the bottom of the container. The unseeded process, on the other hand, maintained stable properties throughout the aging process. Each system had the same amount of surfactant, but the smaller particle system had more surface area to stabilize. The settling occurred as a result of too much additional surface area with no additional surfactant to compensate. This example illustrates the importance of surfactant selection for long-term stability. The smaller particle size can indeed be stabilized, but additional surfactant or a change in the surfactant itself would be required. As shown above, it is clear that the reaction conditions will greatly alter the final product as well. Therefore, it is critical to carefully select the types and amount of surfactants used in the latex as well as the reaction conditions in order to maintain latex stability.

Monomer Composition

Composition of the polymer backbone plays a key role in the use of a polymer. Different bulk monomers impart different characteristics, from frequency of branching to glass transition temperature. These may then manifest in performance shifts in the polymer. Specialty and/or functional monomers can also be added to further modify the polymer and its interaction with its surroundings. Adhesion promotion and hydrogen bonding are common examples of compositional changes to yield the desired final characteristics. Conversely, omitting specific functional monomers can be done to limit interaction.

A polymer system was selected to showcase these results. The top entry of the table below is the control formula which contains a soft monomer, a hard monomer and a polar monomer. An example with a substitution to only the soft, only the hard and only the polar monomer is shown below the control. Finally, two polymers made like the control but with specialty monomers are shown in the final entries of **Table 3** below.

Table 3. Effect of Monomer Selection on Tg and Performance Characteristics

Sample	**Tg (DSC) [ºC]**	**Peel [lb/in]**	**Removability [Peel Failure]**	**Tack [lb/in]**	**Shear [h]**
Control	-44.9	0.31	Clean	0.71	1.28
Soft Monomer	-70.4	0.76	Residue, Ghost	1.06	0.23
Hard Monomer	-45.4	0.08	Clean	0.35	12.78
Polar Monomer	-46.3	0.40	Residue	0.76	0.57
Specialty 1	-45.3	1.52	Clean	1.57	0.15
Specialty 2	-46.4	0.75	Clean	0.92	3.72*

*Shear failure was adhesive, not cohesive, split

By simply varying monomer composition for these adhesives, the overall performance of the final product can be completely altered. This is evidenced by the variation in removability along with differences shown in the peel, tack and shear of the adhesive. For removable adhesives, emphasis is typically placed on the mode of failure of the peel since clean removability is often an end-use requirement. In **Table 3** above, the soft and polar monomer changes show an adverse effect on the removability of the product, resulting in residue or ghosting on the panels. If these particular monomer changes provide some other benefit, it is clear that optimization work would be required to eliminate the residue and ghosting. The range of peel, tack and shear in **Table 3** provides further evidence of the need to study the monomer composition to tailor the product to the end-use requirements.

While a balance of adhesion and cohesion with clean removability are key elements in a removable adhesive, other factors can be manipulated with monomer selection as well. The glass transition temperature of an adhesive is dependent on the monomers selected. This can often limit the selection choices depending on the end-use application. Typically, the glass transition temperature of an adhesive should be 30-70ºC lower than the application temperature [1] to ensure adequate bond characteristics. Therefore, if the adhesive is to perform in a freezer, the application temperature would surely be lower than that of a room temperature application. These considerations should be kept in mind during development to align with the final intended use.

Molecular Weight

Molecular weight is a measurement of the weight of a polymer chain. Manipulation of molecular weight is a classic method for modifying polymer performance. As a general rule, lower molecular weight polymer chains are shorter in length and tend to flow past each other more readily, often resulting in higher bond to a given substrate. Conversely, higher molecular weight tends to create more entanglements in the polymers as they attempt to flow past each other. This typically gives rise to lower initial adhesion that can build over time as more of the polymer chain untangles and adheres to a given substrate. For removable adhesives, control of the polymer flow and bond are critical in designing the polymer. In **Table 4** below, the crosslink density and chain transfer agents are used to manipulate the molecular weight in order to optimize the gel content and performance characteristics of the adhesive.

Table 4. Molecular Weight Effect on Gel Content and Performance Characteristics

Sample	**Crosslink Density**	**Chain Transfer**	**Peel [lb/in]**	**Tack [lb/in]**	**Shear [h]**	**Gel Content [%]**	**MW [amu]**
Polymer 1	High	-	0.31	0.71	1.28	92	990000
Polymer 2	Low	-	0.73	0.94	0.50	89	843000
Polymer 3	Low	Yes	0.77	1.19	0.32	42	79900

The degree of crosslinking and the use of chain transfer agents can be implemented to control molecular weight. This results in drastic changes to the final product. While performance may be of initial interest, the gel and molecular weight are key aspects to be aware of as well. These properties can influence the relative ease with which a polymer may flow. This in turn can cause problems with the wetting of the polymer to various substrates, including the facestock. Delamination of the adhesive is of particular concern since residue from the graphic should be nonexistent. While crosslink density and chain transfer agents are an easy method to influence molecular weight, and thus gel content and performance characteristics, other options could be explored to further fine tune the molecular weight.

Crosslinking

For removable water-based emulsions, crosslinking is another design tool for building structure to the final latex product. There are many different methods of crosslinking, from 1-pot and 2-pot systems, to ambient and heat activated crosslinkers. Application specifics are necessary to better determine how to crosslink a given system based on open times and coating speeds. As an example of crosslinking impact on performance, a polymer system was selected and crosslinked in various manners. All factors were held constant except for the type of crosslinker used, shown in **Table 5** below.

Table 5. Crosslinker Chemistry Versus Performance Characteristics

Sample	**Peel [lb/in]**	**Removability [Peel Failure]**	**Tack [lb/in]**	**Shear [h]**
Crosslinker A	0.31	Clean	0.71	1.29
Crosslinker B	1.52	Clean	1.57	0.15
Crosslinker C	0.75	Clean	0.92	3.72*
Crosslinker D	0.59	Clean	0.93	42.33*
Crosslinker E	0.96	Clean	1.41	2.68

*Shear failure was adhesive, not cohesive, split

Based on the spread of performance attained from the same system, it is clear that crosslinking is a key attribute to consider when varying polymer performance. For the purposes of the study in **Table 5** above, the relative amount of crosslinker is unchanged for each polymer. The emphasis of the results above is placed on the actual chemistry of the crosslinker that was used. As indicated in the prior section on molecular weight, the crosslink density itself can be altered to further adjust the performance properties.

Crosslinkers C and D both indicate adhesive failure during shear tests. This suggests that the cohesive strength of these adhesives is so high that the polymer will not fail cohesively. Conversely, Crosslinker

B appears to be an ineffective method for building cohesive strength. If a polymer system lacks cohesive strength, the risk of the adhesive leaving residue upon removal increases. In the examples above, none of the systems left residue, but it is critical to design as much margin of error into the system as possible.

Results & Discussion

With the categories and examples shown above, the next step is to tie these properties together to build a polymer structure that fills a need in the market. Each of the above structure-property relationships has been treated as an individual mechanism, but in reality each one builds off the others. A change in crosslinker can cause a shift in molecular weight, or a shift in surfactant selection may cause destabilization of a particular monomer composition. In designing new polymer systems, those skilled in the art must constantly be on guard for positive or negative interactions between these variables.

With an understanding of the cause and effect of the structure-property relationships above, the application requirements for the market must be reviewed first. Vinyl graphics is a large market space that continues to evolve as new adhesive and vinyl constructions are brought to the market. In order to design a system for these needs, many performance factors must be balanced. For this discussion, removable adhesives are the primary focus. A good removable will maintain its performance throughout its lifetime on the final application and will remove cleanly with no residue. The removal of the adhesive should not be jerky or zippy; rather, it should be smooth and consistent. Varying degrees of bond may also be beneficial, depending on how tight the graphic must adhere to the surface and how rough or dirty the surfaces that could interfere with the adhesive may be. Aged performance off the coated facestock must also be considered. Since PVC films contain plasticizers, the migration of these components must not interfere with the final adhesive product. Often the plasticizer migration leads to a loss in peel and shear [3]. To test for the aged performance, the liner/adhesive/facestock construction is often placed in an oven for a week to simulate long-term storage. This gives additional time for the plasticizer to migrate into the adhesive, serving as a good test in bond retention when the aged construction is re-tested. Finally, the adhesive must maintain stable shelf-life and will need to be transfer coatable so as to eliminate sending vinyl facestock through an oven, potentially damaging the vinyl itself.

With the requirements listed above, several polymer systems to follow showcase potential use in the market. Vinyl is the intended facestock, but additional testing was conducted on polyester (PET) as well due to its prevalence as a standard in the industry. In **Figure 1** below, a potential candidate adhesive is shown.

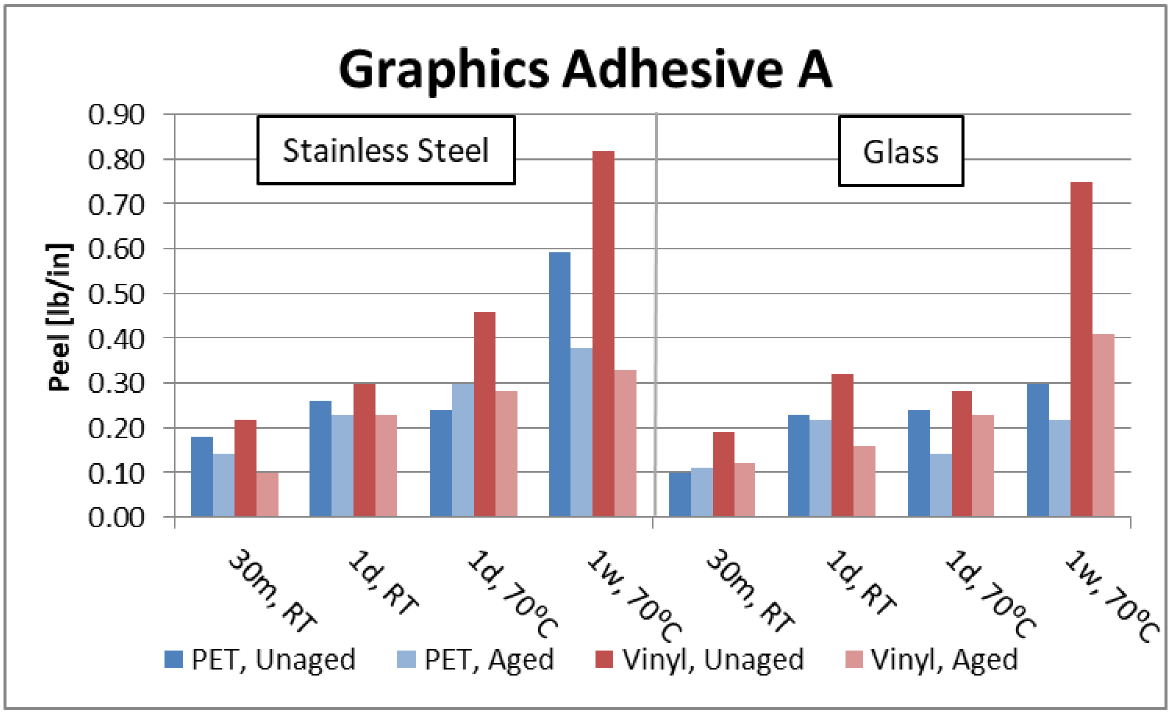

Figure 1. Peel Performance Comparison of Graphics Adhesive A

The prototype graphics adhesive shown above maintains a low bond across full aging treatment. As the adhesive dwells on the panels for longer periods of time, the bond continues to build for both vinyl and polyester testing. However, in comparing the aged adhesion to the unaged adhesion for vinyl and polyester, the long-term retention of the aged adhesive bond is much lower than the unaged bond. Since the aged bonds are lower than the unaged bonds, this particular adhesive could face problems with in-field failure if the adhesion is insufficient. While this first prototype shows promise, another adhesive candidate is compared below.

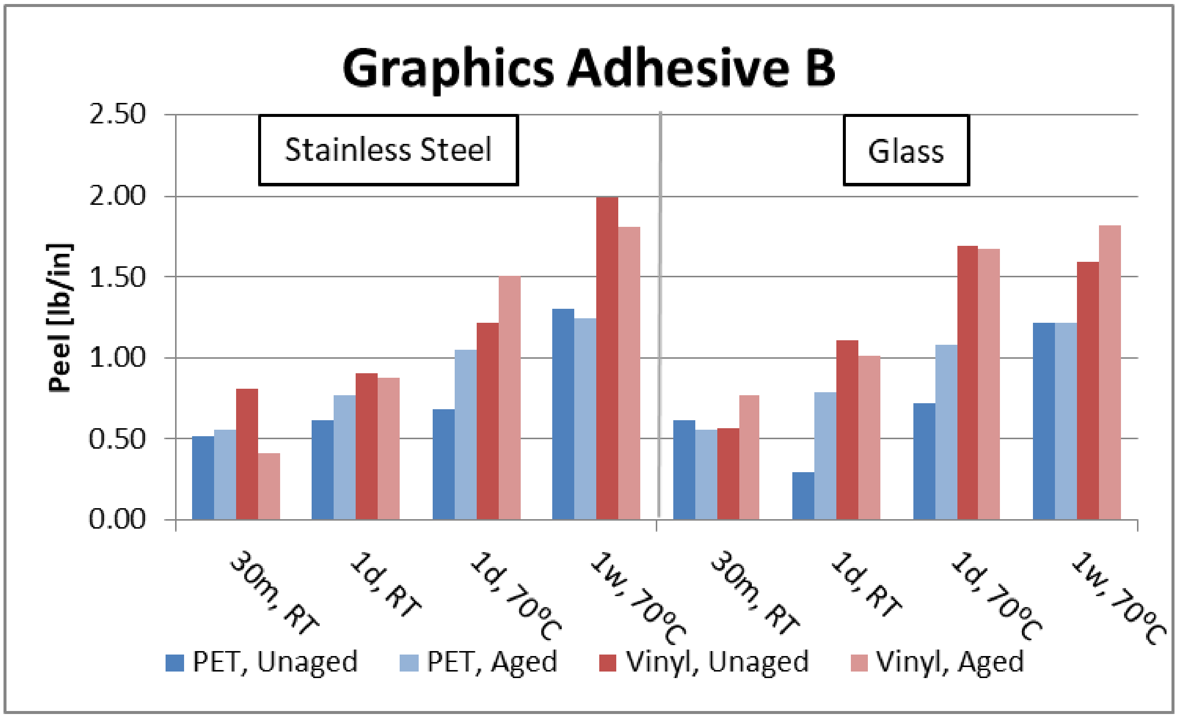

Figure 2. Peel Performance Comparison of Graphics Adhesive B

This prototype is a modification of Graphics Adhesive A, with several of the structure-property relationships discussed in the initial sections altered to modify long-term aging performance. Comparing **Figure 2** to **Figure 1**, it is clear that the bond in Graphics Adhesive B is much higher than Graphics Adhesive A throughout the aging tests. It is noteworthy to compare the aged and unaged bond for the two adhesives. Where Graphics Adhesive A fell short on aged adhesion, Graphics Adhesive B has a different result. Both the aged and unaged adhesion values for Graphics Adhesive B are nearly identical in **Figure 2**, suggesting that this type of approach will result in an improvement in the long-term stability of the adhesion. Neither the PET nor the vinyl results indicate an appreciable loss in performance during aging. This indicates that Graphics Adhesive B is a great contender for plasticizer resistance and therefore a suitable adhesive for vinyl products. The drawback to this adhesive would be in the bond itself – if lower adhesion is needed for the application, an adjustment to the structure-property relationships will need to be made to bring the adhesion values down.

Conclusions

The prototype adhesives shown in the figures above are examples of using the structure-property approach in building polymer systems to meet market needs for removable adhesives. From understanding the control of adhesive performance via structure-property relationships, manipulation to meet customer needs is more straightforward. Typically, an initial design to explore some of the properties above can yield an overview of the design-space being analyzed. If performance properties critical to the success of the adhesive are not readily influenced in this space, a new design to explore other materials will be needed. Once a system that can vary each performance metric is found, optimization can be performed to maximize performance. In doing so, the most critical performance properties can be dialed in for customer needs. By designing adhesives with structure-property relationships in mind, the complicated intricacies of polymers can be simplified, allowing progress to be made, resulting in a successful adhesive.

With a fundamental understanding of the structure-property relationships to control adhesive performance, the design approach to achieve customer needs can be improved. As new demands from regulations and new needs in the market arise, these principles guide the design approach to reduce time to market. While these studies have improved understanding of structure-property relationships, they are by no means an all-encompassing view of development efforts. Perhaps in the future the field of polymer science will move towards computational models that can predict with greater accuracy the final properties, but until that day arrives wet chemistry on the bench is a necessity. As we strive to improve water-based technologies for a brighter, greener future, we hope this review will benefit the development efforts of others.

Appendix

In order to characterize the adhesive performance of the samples shown throughout the paper, a set of standardized testing procedures was used. These standardized testing procedures can all be found in the 16th edition of Test Methods for Pressure Sensitive Adhesive Tapes, published by PSTC. All peels were conducted according to the method set forth under PSTC-101. Loop tack was conducted using the method set forth under PSTC-16, and shear was conducted using the method set forth by PSTC-107. All performance testing was completed in a controlled temperature and humidity room of 70 +/- 3ºF and 50 +/- 2% relative humidity. These conditions fall within the “standard conditions” listed in Appendix A of the aforementioned testing manual. Lastly, surface preparation of the test panels followed the recommended cleaning procedure listed in Appendix B of the aforementioned testing manual. All testing was conducted following these guidelines in good faith, minimizing any deviation from the procedure as accurately as possible.

References

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