



NOVEL CYANOACRYLATE-BASED PSA FOR SEMI-STRUCTURAL APPLICATIONS

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Abstract

A market need exists for a semi-structural adhesive solution in an easy to use form. Current adhesive solutions are difficult to apply and do not allow for design flexibility. Existing high-performance tape options do not approach the bond strength required in many applications. This paper will discuss an innovative cyanoacrylate-based solution that provides superior bond strength with the ease-of-use of a PSA tape. The processing and performance benefits of this developmental technology compared to existing technologies will be presented.

1.0 Technology Background

1.1 Cyanoacrylate Technology

Cyanoacrylate instant adhesives, also known as “Superglues” [1], are an important class of materials that have found extensive use in industrial and consumer markets, owing to their rapid cure speed at ambient temperature, ease of use, and excellent adhesive strength on a range of common substrate surfaces such as metals, plastics, rubbers, woods and ceramics [2]. As cyanoacrylate adhesives are applied as liquids, they exhibit a rapid rate of polymerization, which allows them to rapidly bond two surfaces together that form high bond strengths that can be handled within seconds to minutes. It is this convenience of use that makes them considerably attractive as an adhesive having found utility serving a range of markets including general industrial assembly, consumer, electronic, medical and tissue bonding and engineering sectors globally. Figure 1 shows the more commonly commercially available 2-cyanoacrylate esters, which are produced industrially by a Knoevenagel condensation of paraformaldehyde with an alkyl cyanoacetate under base catalyzed conditions [3].

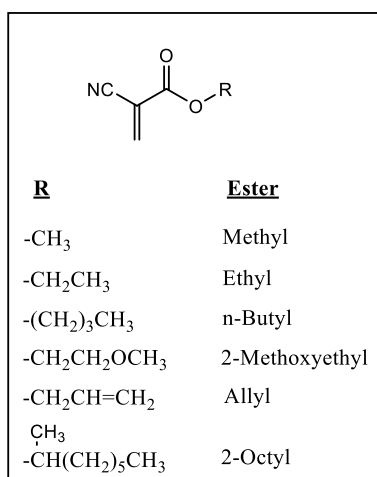


Figure 1. Typical Cyanoacrylate Esters

Cyanoacrylates are incredibly reactive systems, attributed to the strong electron-withdrawing nitrile (CN) and ester (CO₂R) groups attached to the α -carbon of the double bond, making β -carbon very susceptible to polymerization by nucleophilic or anionic species. In an adhesive context, anionic polymerization is the most common and important mechanism to cure the adhesive system. Owing to this inherent reactivity, cyanoacrylate adhesives differ significantly from other reactive systems in that they rarely contain significant amounts of co-reactants or additives to improve the overall adhesive properties [2]. As stated above, and shown in Table 1, there are several reasons why cyanoacrylates are attractive as adhesives. However, there are some performance limitations such as limited heat durability, poor cure through gap (high thicknesses) or gap filling ability, coupled with difficulties

around up-formulation of the base adhesive system with performance enhancing additives that prove challenging to position cyanoacrylates into new and alternative application areas.

More recently, the development of an innovative structural-cyanoacrylate hybrid technology has addressed some of the performance limitations shown in Table 1. Considering the clear property enhancements that were achieved through the development of this hybrid adhesive system, the focus was then turned to ideation of a pressure sensitive- cyanoacrylate (PS-CA) hybrid technology.

Table 1. Key Advantages and Limitations of Cyanoacrylate Adhesives

| Advantages | Limitations |
|----------------------------------|--|
| Room Temperature Cure | Monomer and additive selection are limited |
| Fast Curing | Limited Gap Filling |
| Multi-substrate Bonding | Poor thermal durability (<120°C) |
| Rapid Green Strength Development | Brittle Polymer |

1.2 Pressure Sensitive Adhesive Technology

An adhesive is considered to be pressure sensitive when it exhibits tack at room temperature, forming a strong bond with only a slight pressure—finger pressure—without the need for further activation [4]. These characteristics turn pressure sensitive adhesives into products of convenience. They have suitable cohesive strength to hold the bond they form; however, the bond strengths do not approach those of the aforementioned cyanoacrylates.

Pressure sensitive adhesives can be categorized according to their base chemistry: solution acrylics, emulsion acrylics, solution rubber, hot melt, UV acrylics, and silicones. Each one of these categories has their own strengths and limitations regarding environmental friendliness, machinability, and end-use performance. However, in general, pressure sensitive adhesives can be said to share the following characteristics when compared to a liquid cyanoacrylate adhesive:

Table 2. Key Advantages and Limitations of Pressure Sensitive Adhesive Films

| Advantages | Limitations |
|--|--|
| Easy to handle, readily bondable | Limited cohesion |
| Good initial peel | Size of die-cut parts limited by bond strength |
| Consistent application of adhesive thickness | |
| Possible Repositionability | |

Being versatile and ready to bond, pressure-sensitive adhesives (PSAs) are used not only in industrial settings but in consumers’ day-to-day life as well. In general, the marketplace in which PSA’s are present can be divided in 4 categories:

Table 3. Pressure Sensitive Adhesives Marketplace

| Market Category | End-use Examples |
|-------------------------|---|
| Labels | Food and Product Labels, Logos, Equipment Marking, Shipping Labels |
| Graphics | Vinyl and Reflective Signage, Vehicle Wrapping, Shelf Marking, Protective Films |
| Tapes | HVAC, Automotive, Electronics, Sports and Medical |
| Medical and Transdermal | Bandages, Surgical Drapes, Device Assembly, EKG Pads, Drug Delivery |

Focusing on the tape marketplace and depending on the end-use, a tape can be constructed as a transfer tape, double coated tape, foam tape or a single coated film tape. For this particular paper, as shown in Figure 2, the PS-CA hybrid tape can be considered as a transfer tape given that the adhesive is coated between two liners and is used without a carrier in the application.

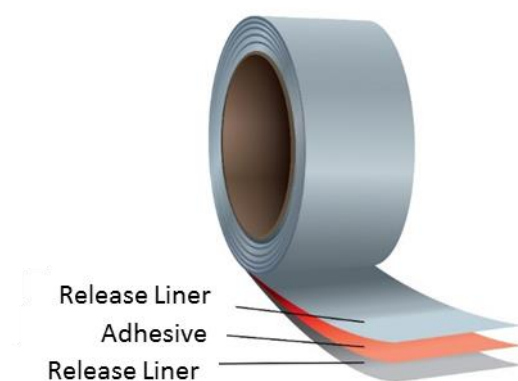


Figure 2. Example of a Transfer Tape construction

2.0 Technology Development

2.1 Technical Concept

As clearly highlighted in the last section, there are several advantages and limitations for independently using PSA and cyanoacrylate-based adhesives. Leveraging significant technical expertise in both technologies was critical in the development of a PS-CA hybrid adhesive. Figure 3 summarizes the concept behind this hybrid project: to provide the performance of a liquid semi-structural adhesive in an easy-to-use tape-like film.

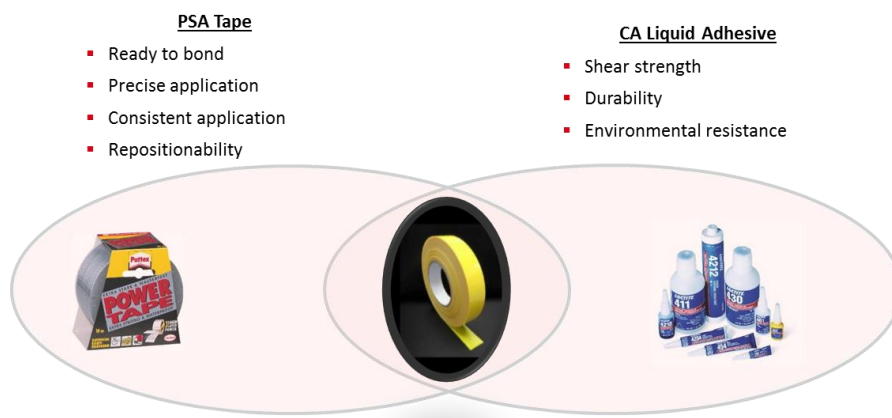


Figure 3. Summary of Concept behind a PS-CA Hybrid System

The initial approach was to develop solvent-based pressure sensitive systems utilizing ethyl cyanoacrylate (ECA) monomer. Initial studies focused on the formulation of ECA with suitable film formers (polymers) and additives known in the PSA field. The team encountered several difficulties as the PSA materials exhibited incompatibility and solubility issues with the cyanoacrylate, with undesirable polymerization occurring in all cases. An extensive screening program was established to find a suitable polymer system that would be compatible and soluble in the cyanoacrylate/solvent system, while still maintaining the tack features of a PSA once coated and dried into a thin film.

Several key polymers were identified which showed good solubility characteristics in the cyanoacrylate and enabled some initial coating studies. Coatings were applied onto a siliconized-PET release liner, followed by covering with a polyethylene release liner, to limit moisture exposure, once the solvent had been evaporated off. However, despite the team's best efforts it proved incredibly challenging to get consistent coating that maintained any stability after 30 minutes. The liquid monomer underwent phase separation from the polymer matrix and polymerized rapidly. Several strategies were employed where the acid stabilization level of the ECA was increased and the viscosity of the adhesive modified; however, increasing the viscosity to avoid phase separation affected the ability to coat the wet adhesive. The addition of the increased acid stabilizer reduced the monomer reactivity and thus, polymerization was no longer instantaneous.

The team then considered the development of solid cyanoacrylate monomers. The key questions were:

1. Was it possible to prepare a cyanoacrylate solid monomer?
2. Could the properties be tailored such that the monomer would be solid at room temperature but liquid when heated to allow formulation and coating?
3. Could a good balance of stability and reactivity be achieved in a solid format?

Several monomer types were identified from literature; however, it was decided to prepare phenylethyl cyanoacrylate (PhECA), structure presented in Figure 4, as it has a melting point of 91°F. A melting point of 91°F would be ideal for formulation into a solvent-based PSA, possibly enabling the material to solidify in the coated format, giving increased stability as well as no phase separation issues and a decent coating performance. PhECA was successfully prepared via Knoevenagel condensation of paraformaldehyde and phenyl ethyl cyanoacetate to yield the pure PhECA monomer.

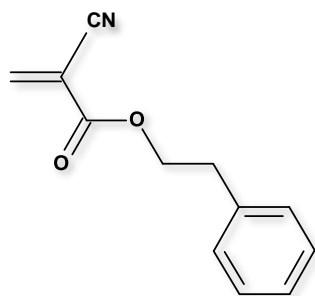


Figure 4. *PhECA Monomer Structure*

The team then used the same base formulations as used for the ECA study, however substituted it with the solid PhECA monomer. It was found that by changing from the liquid monomer to the solid monomer, that the adhesive's coating was possible and its stability achievable. Interestingly, the PhECA monomer was able to polymerize nicely when applied to numerous substrates inside the PSA matrix. The team comprised of leading experts in cyanoacrylate technology development, deemed this slight modification on the monomer set surprising and inventive with subsequent patent applications filed.

2.2 PS-CA Adhesive Performance

Evaluating the performance of a PS-CA adhesive in its final tape form utilizing standard PSA test methods such as peel, shear, or tack, presented some difficulties. It is important to consider that while the adhesive is considered a PSA in its initial state, the tape does not behave like a PSA after the curing step. Moreover, facestock considerations become more complex than usual when considering the interaction with the reactive nature of this adhesive. In fact, the PS-CA hybrid system is primarily intended as application of a part bonding adhesive rather than a traditional tape.

While the mechanical properties of the facestock affect any tape's performance, the pH and hydrophilic properties of a facestock can be crucial for the proper curing of a PS-CA-based tape. To illustrate this dramatic impact of the facestock on the PS-CA tape's performance, shear adhesion was evaluated according to Procedure A of PSTC-107 [5] with the addition of a cure step of 1 hour at 140°F after samples had been rolled onto stainless-steel panels. The area of contact was 1-inch-high by 0.5-inch-wide with 40 grams per square meter (gsm) adhesive coat weight. The test was conducted with a 2000g load in a controlled room temperature and humidity chamber. The only difference between the test specimens was the facestock: one used PET and the other used aluminum. The performance contrast is shown in Figure 5: when transferred to PET, the cure of the adhesive is significantly diminished so that bond strength is not achieved.

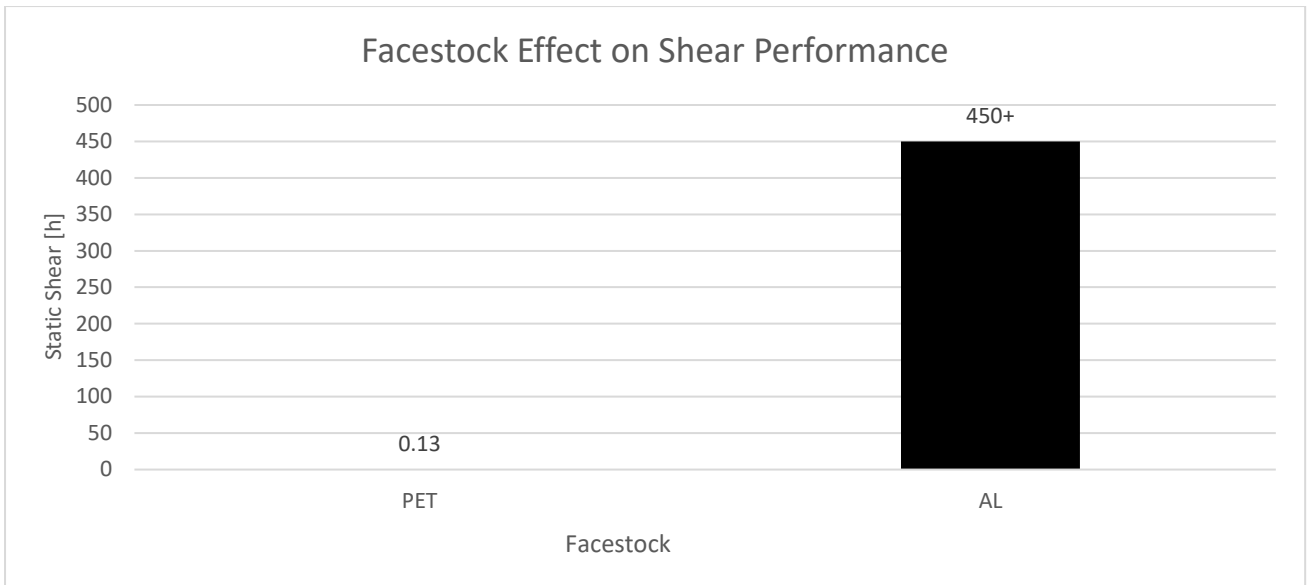


Figure 5. Facestock Effect on Shear Performance

As mentioned above, testing the PS-CA adhesive using standard PSA methods had its own challenges, resulting in inconsequential data sets. Therefore, the primary evaluation method of the PS-CA adhesive consisted of pulling room temperature 1 sq. in. lap shear bonds at 0.5 in/min. as shown in Figure 6. The bonds were prepared using free film adhesive coated with 40 to 50 gsm. To provide an ample vision of the adhesive’s capabilities, the coat weight, substrates, cure conditions and aging conditions were varied through the testing sets.



Figure 6. Lap Shear Test Specimen Examples

Similar to facestock impact on shear performance, the test surface substrate will also affect the PS-CA adhesive’s cure and the bond strength as shown in Figure 7. All samples within this data set were cured for 1 hour at 140°F. The PS-CA adhesive resulted in great adhesion to metals like aluminum and steel. When considering plastics, strength for ABS bonding is still considerably strong while lower surface energy plastics, such as polypropylene, HDPE, and LDPE, result in very poor bond strengths. As with other cyanoacrylates, it is expected that bond strength should increase with the use of a primer when adhering low surface energy materials. Lastly, the PS-CA adhesive wet into the wood surface, barely leaving any adhesive on the interface. It is to be determined whether an increase in coat weight could enhance the bond strength when working with wood substrates.

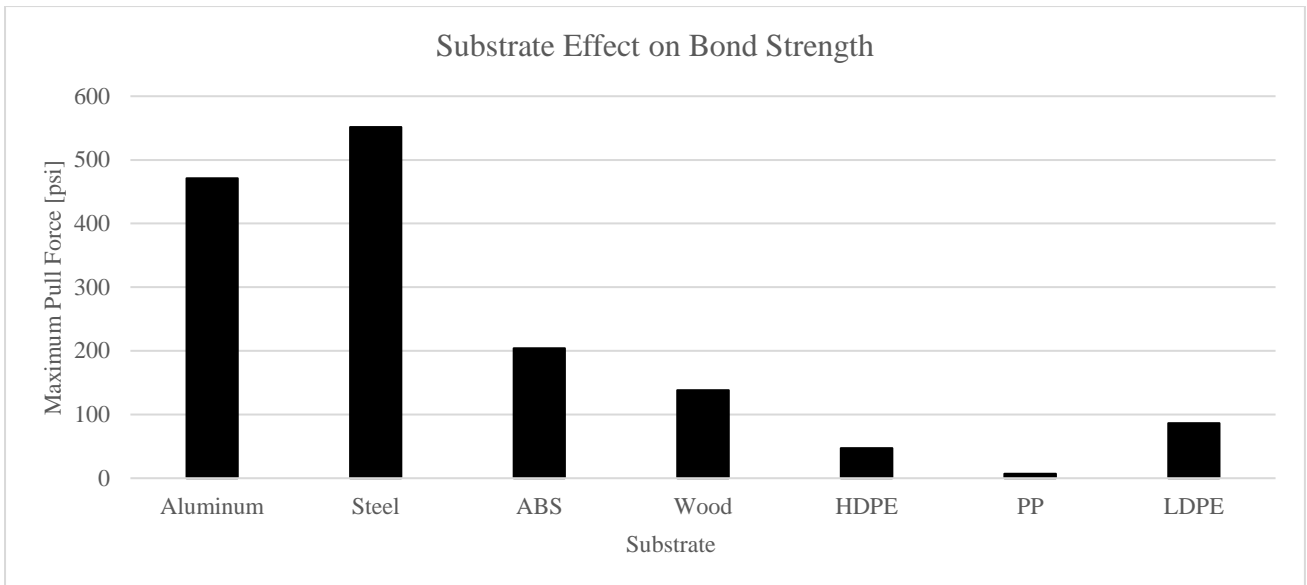


Figure 7. Substrate Effect on Bond Strength

The effect of adhesive coat weight on bond strength was tested on three different substrates: ABS, aluminum, and steel. Two different coat weights were tested: 50 gsm and 150 gsm.

As shown in Figure 8, a higher coat weight does not translate into a higher bond strength. Inherent to their nature, cyanoacrylates are known to be poor at curing at high thicknesses (gaps). Based upon this theory and results, it is recommended to look for optimum bond strengths at the lower coat weights—between 40 and 50 gsm in this case.

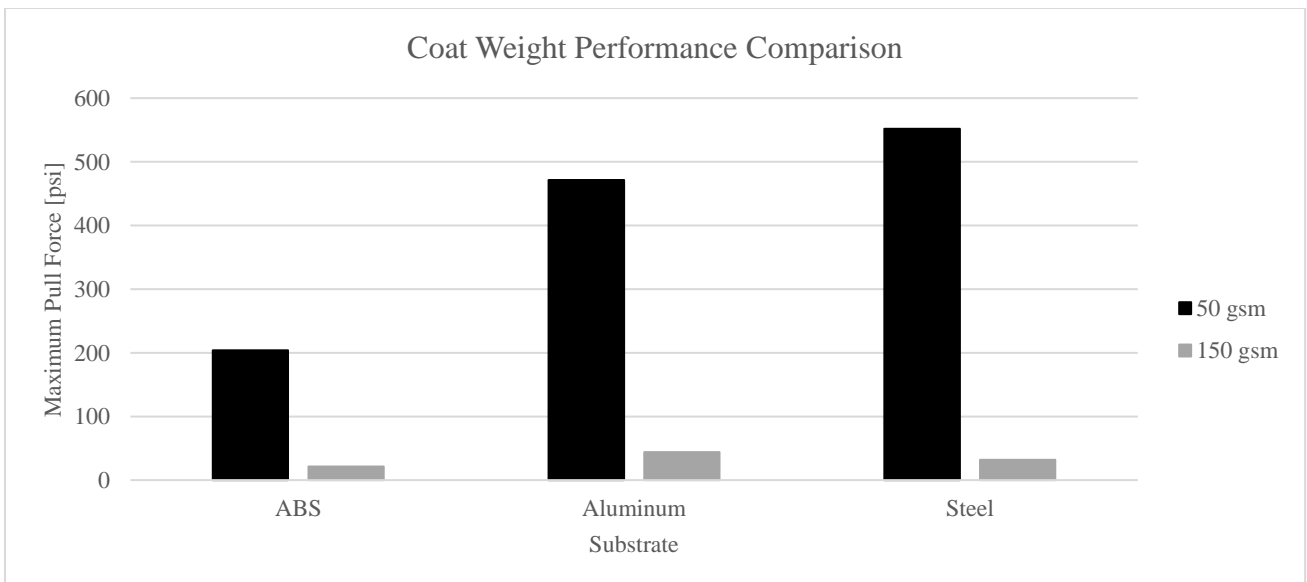


Figure 8. Coat Weight Performance Comparison

The data presented thus far was gathered using a cure condition of 1 hour at 140°F. Other cure conditions were explored; however, optimum bond strength was achieved after conditioning the samples at 140°F for 1 hour followed immediate testing as shown in Figure 9.

The addition of heat during the cure step pushes the cyanoacrylate portion of the adhesive into a liquid form, and therefore, reduces the time required to achieve a high bond strength. It is expected that, if left to cure for a prolonged time, the room temperature cure curve would eventually merge with the added-heat cure curve.

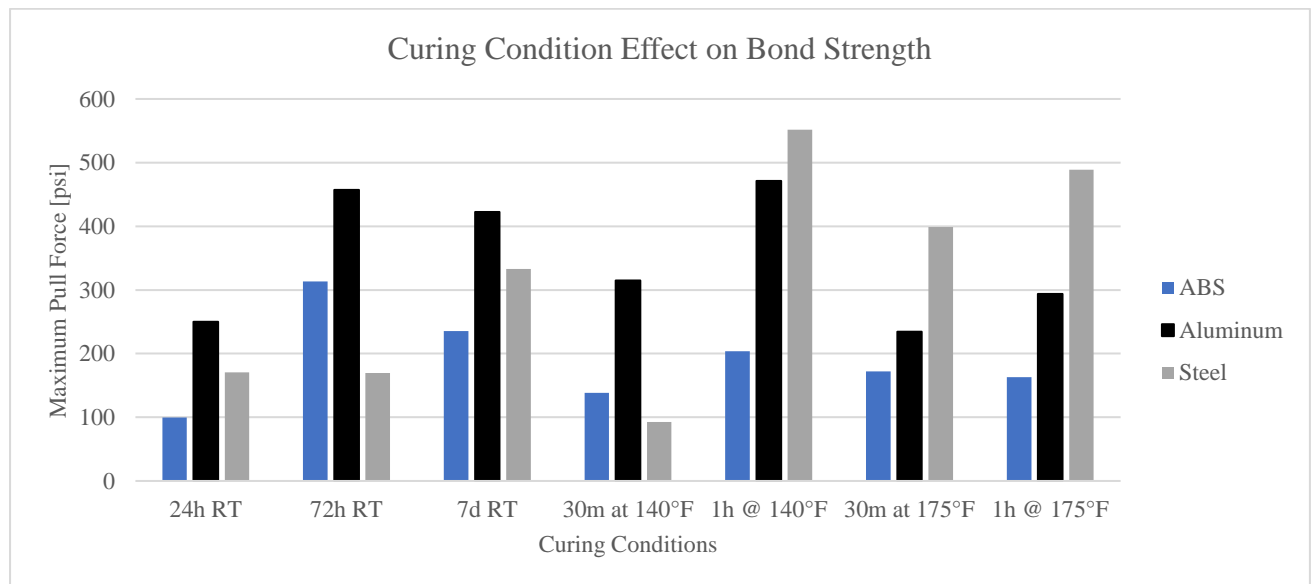


Figure 9. Curing Condition Effect on Bond Strength

Given that the PS-CA adhesive showed great performance for metal bonding at room temperature, the next step was to explore the potential service temperatures of the adhesive using a metal substrate, therefore, aluminum samples were tested after being subjected to different environmental conditions. The coat weight was kept constant between 40 and 50 gsm and samples were cured for 15 minutes at 250°F.

Second, it is important to specify that after being conditioned for 7 days, the samples were given a 1-hour recovery time and were pulled at room temperature, not at the aging environmental conditions. That said, at low temperatures, if not given an opportunity to recover, specimens will result in adhesive failure, breaking without much effort, resulting in a low strength bond.

Third, as observed in Figure 10, results suggest that the PS-CA adhesive can withstand both high and low temperatures, yielding a slight advantage in a higher humidity environment—a condition which can prove difficult for other pressure sensitive adhesives.

The next section will further compare and contrast the main similarities and differences between the PS-CA adhesive and other more conventional pressure sensitive adhesives.

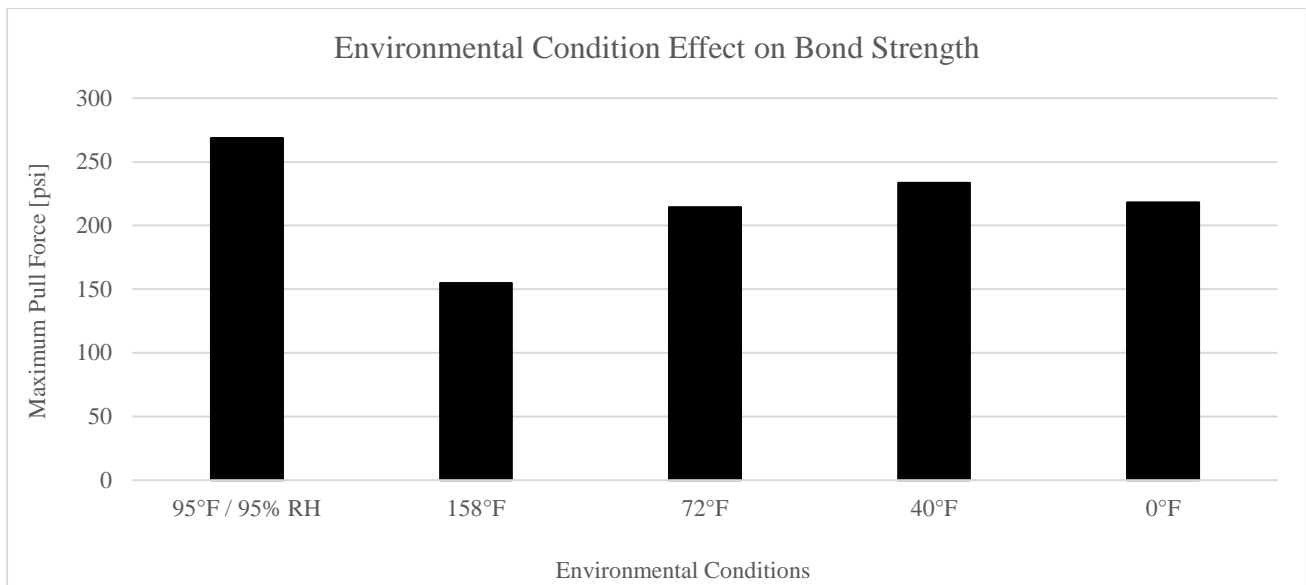


Figure 10. Environmental Condition Effect on Aluminum Bond Strength

2.3 PS-CA versus Conventional PSAs

The PS-CA adhesive has physical properties comparable to other solution acrylic PSAs: a transparent, colorless appearance with a solids content of 48-52 percent at a viscosity of 2,000 to 6,000 cP at room temperature. However, unlike solution acrylic PSAs, when not in use, the PS-CA adhesive must be stored under refrigeration, protected from moisture exposure, and allowed to come to room temperature prior to opening the container. Being a solvent-based adhesive, PS-CA must be stored away from open flames and other sources of ignition.

The PS-CA adhesive can be coated by any conventional roller technique appropriate for the product's viscosity. Extra care should be taken during the drying step to avoid degrading the cyanoacrylate polymer. A drying temperature of 140°F is recommended, and should not exceed a temperature of 195°F for more than 3 minutes. Once coated, the PS-CA coated film can be used in automated application processes.

Whenever coating the PS-CA adhesive, its reactivity should be taken into account while considering the appropriate release liner system for an application. For example, when coated on a paper liner, the moisture retained by the paper can promote premature polymerization of the cyanoacrylate component of the adhesive, rendering it unusable. Lab coatings proved that the adhesive film loses its tack as soon as two weeks after coating the PS-CA onto a paper liner. Conversely, coating onto a siliconized PET and PE film release liners allows the adhesive to maintain stability for about six months.

To achieve this full 6-month shelf life, the PS-CA film should be stored between 35°F and 47°F, preferably in a sealed pouch. It is unproblematic to keep the tape at room temperature during application as long as it is returned to cooled conditions after use. If an application requires different handling and storage conditions, appropriate evaluation must be carried out considering that the adhesive's shelf life and end-use performance can be compromised.

As previously discussed, comparing the end performance of the PS-CA adhesive to that of conventional PSAs is difficult, as the PS-CA bonds are destructive in nature. A series of lap shears were pulled at room temperature at a speed of 0.5 in/min, using a 40 to 50 gsm coat weight free films of different adhesive chemistries on multiple substrates. The PS-CA samples were cured for 1 hour at 140°F and left to wet out overnight along with the rest of the PSA samples prior to testing. Figure 11 illustrates the superior bond strength of the PS-CA across a variety of substrates. It is worth noting that

the failure mode shown by all samples (except for PS-CA) was mostly adhesive with some instances of cohesive failure. However, for the PS-CA samples, the bond was maintained until it destructed yielding a loud “clack” when the bond was broken—no panel sliding was observed until after the noise was heard and the bond was broken.

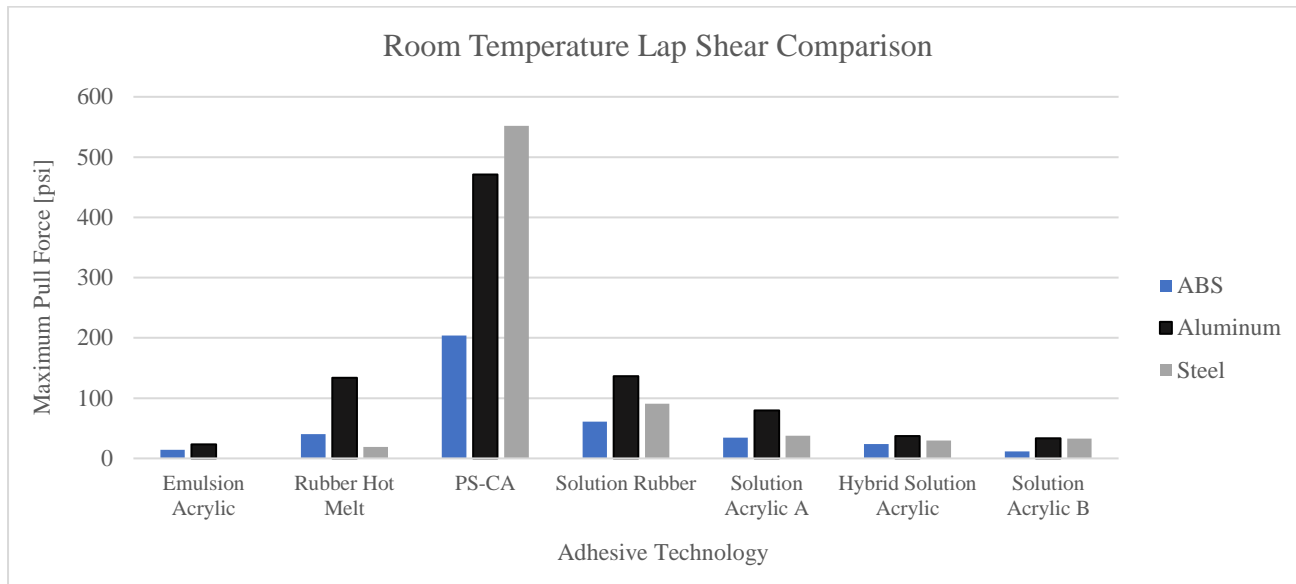


Figure 11. PS-CA Lap Shear Performance Compared to Conventional PSA Chemistries

For testing the tape’s high temperature limits under a constant 1000g applied load, shear adhesion failure temperature (or SAFT) was tested per PSTC-17 [6]. An aluminum foil facestock was used for the construction of these samples with a 40 to 50 gsm coat weight. After rolling samples onto stainless steel panels, the PS-CA specimen was cured for 1 hour at 140°F. As shown in Figure 12, even though the cyanoacrylate is expected to degrade at high temperatures, the SAFT value for the PS-CA adhesive was comparable to those values observed for other PSA chemistries, where solution acrylic A represents a general-purpose adhesive and solution acrylic B is a high temperature adhesive.

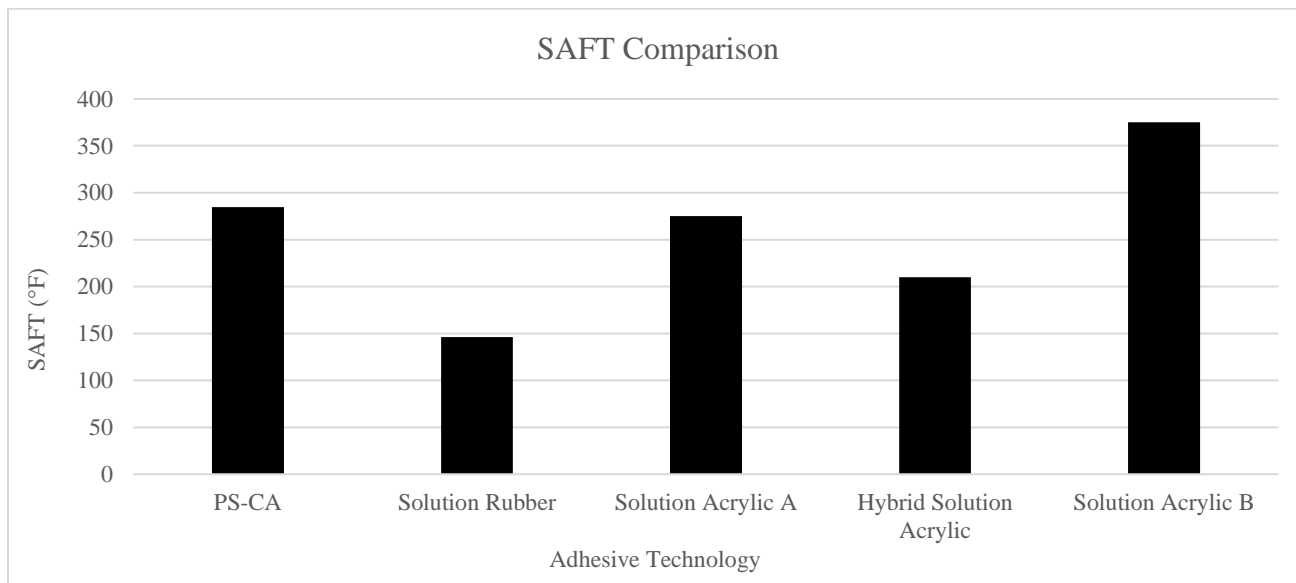


Figure 12. PS-CA High Temperature Performance Compared to Various PSA Chemistries

3.0 Technology Value Proposition

As of today, there is no commercially available solution for a PSA product with semi-structural bonding strength. Hybrid pressure sensitive cyanoacrylate (PS-CA) technology achieves bond strengths that are orders of magnitude greater than high performance acrylic tapes available commercially today as discussed within this paper and depicted in Figure 13.

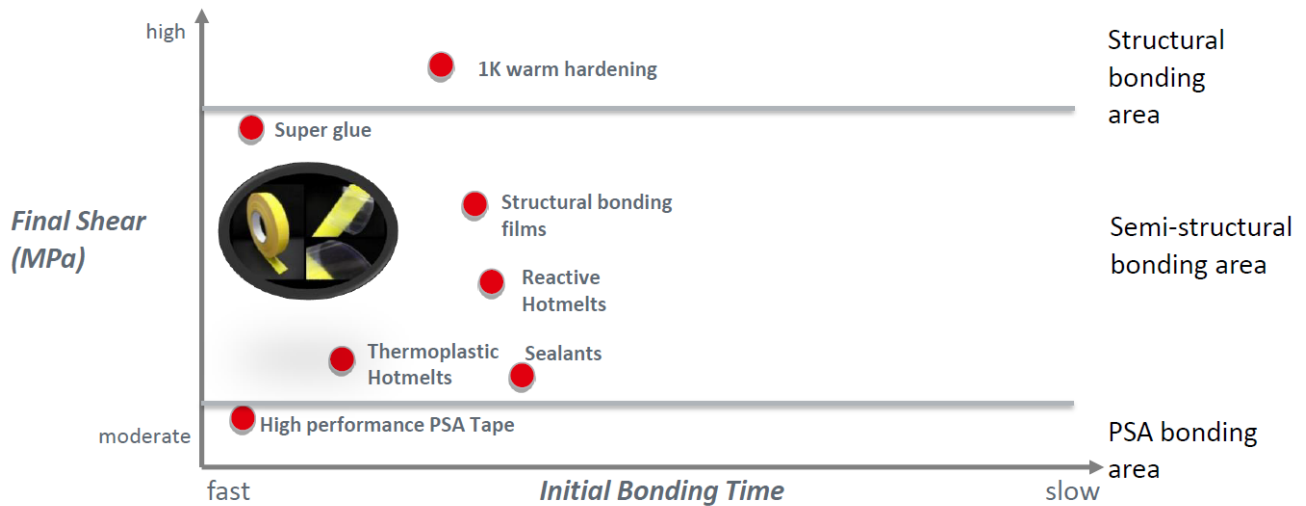


Figure 13. PS-CA Performance Landscape Relative to Other Adhesive Technologies

The increased bond strengths possible with PS-CA technology enable pressure sensitive adhesives to be used in demanding industrial assembly applications such as automotive, electronic device assembly, and building components. These applications are increasingly demanding more reliable processes, higher bonding strength for smaller parts, and precise bonding solutions. The PS-CA technology addresses all these concerns. Unlike the application of liquid cyanoacrylates, PS-CA adhesives can be applied at the same adhesive deposition (coat weight) each time via reproducibly coated tape rolls. As seen in Figures 11 and 13, high performance acrylic tape products do not approach the bond strength of PS-CA. The increased bond strengths with the PS-CA technology addresses the market demand for higher bonding strength for smaller parts. Lastly, in response to more precise bonding solutions, PS-CA's ability to be die-cut and handled as a film with initial repositionability enables precise placement that cannot be achieved with liquid adhesive solutions.

Acknowledgements

Marissa Phelan, project manager for the PS-CA project, for her unlimited knowledge transfer.

Allison Luciano, technical service manager, for her mentorship through the process of testing the product and writing this paper.

Michael Krejsa, technical service manager, for his support with this project.

Howard Yun and Thomas Silva, applications engineers, for sharing their insight on their respective areas of expertise.

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