HYBRID ADHESIVE DEVELOPMENT FOR HIGH PERFORMANCE TAPE BACKINGS

Cynthia Cain, Sr. Materials Scientist, Custom Laminating Corp, Mt. Bethel, PA
Julie Pankowski, Research Chemist, Custom Laminating Corp, Mt. Bethel, PA
Michael Zajaczkowski, R&D Director, Custom Laminating Corp, Mt. Bethel, PA

Abstract

High performance industrial laminates are achieved through a novel waterborne adhesive system where previously only solvent-based systems were suitable. A miscible hybrid blend of urethane and acrylic polymers with a single glass transition temperature (Tg) provides excellent adhesion to various substrates, including olefins, foil, and polyester. The adhesive enhances the elongation properties and environmental resistance of the laminates. These laminates are commercialized in applications such as construction tape, exterior flashing, and roofing underlayment, which require strength properties like puncture and tear resistance. New tape backings are being developed for barrier, energy storage, and wire harness applications. In addition to the performance advantages of this adhesive, this sustainable VOC-free solution will have a positive impact on life cycle analysis.

Introduction

Achieving solvent-based adhesive performance with water-based adhesives is a common goal of adhesive formulators. Water-based adhesives are a sustainable alternative to solvent-based adhesives, providing improved health and safety and reduced volatile organic compound (VOC) emissions. The market for water-based adhesives is expected to have continued growth over the next decade due to increasing environmental regulations and growing consumer interest in sustainable goods.[1] A significant limitation of water-based adhesives is that they tend to have inferior durability compared to solvent-based adhesives, which can greatly hinder their use in high performance industrial laminates.

Both polyurethanes and polyacrylates are useful as laminating adhesives and pressure sensitive adhesives (PSAs). Polyurethane dispersions (PUDs) are known to have good weatherability, chemical resistance, and adhesion to a wide variety of substrates. To achieve these properties, PUDs often require co-solvent and high levels of crosslinker which limits adhesion and elongation. Advantages of polyacrylate emulsions include good film formation relative to PUDs without the addition of co-solvent, excellent UV resistance, higher elongation, and lower cost. Waterborne polyacrylates have lower modulus and tensile strength relative to PUDs and contain surfactants which degrade water resistance.

Although blends of polyurethanes and polyacrylates are known, they are characterized as 1) phase separated blends where distinct phases exist either in discreet domains or in core-shell morphologies or 2) as copolymerized grafted polymers. Researchers have found that physical blends often have performance that is even lower than what would be predicted from an arithmetic rule of mixtures, likely due to the incompatibility of the two polymers.[2,3]

Therefore, it is beneficial to provide an adhesive formed by a compatible mixture of polyurethane and polyacrylate polymers, which leads to a miscible hybrid polymer system. Benefits of such a system include reduced cost, a wider formulation latitude, and improved environmental resistance without

involving complicated grafting reactions. By utilizing a water-based polyurethane dispersion (PUD) and an acrylic emulsion to create a hybrid waterborne adhesive, the performance limitations of waterborne adhesives can be overcome.

Experimental

Materials

The untackified formulation consists of two base polymers: a larger particle size, low Tg acrylic emulsion optimized for excellent water resistance, and a small particle size, self-stabilized polyurethane dispersion for durability. The PUD's small particle size contributes to excellent film formation. Additionally, the formulation includes an isocyanate crosslinker for improved heat resistance. This formulation is suitable for film-to-film constructions, including polyester and polyolefins, such as polyethylene and polypropylene. To further enhance the performance of this adhesive on aluminum foil constructions, a rosin ester tackifier dispersion is added. The physical properties of these materials are listed in Table 1. The viscosity of the hybrid blend is lower than either of the components individually due to the bimodal distribution of particle size.

Table 1. Physical Properties of Adhesive Materials

Material	Viscosity (cP)	pH	Solids (%)	Tg[a] (°C)
Acrylic	962	7	59	-30
Polyurethane	400	8	45	-44
Rosin Ester Tackifier	10	8	58	~55[b]
Isocyanate Crosslinker	--	N/A	100	N/A
Acrylic-Urethane Blend	212	8	51	-37

[a] Tg was determined by DMA peak tan δ.
[b] The Tg of the tackifier is estimated as half the softening point of 110°C.

According to the concept of Gibbs Free Energy, physical blends of polymers are usually incompatible due to their very low entropies of mixing, which is related to their high molecular weights. This incompatibility is the driving force for the polymers to separate into different phases with particles that are large, inhomogeneous and have poor interfacial adhesion. For these reasons, two-phase morphologies usually result in poor physical properties.[4] Superior physical properties can be obtained with compatible blends, which can be achieved if the system has a negative enthalpy, presumably associated with hydrogen bonding interactions between the polymers. The polymer blend listed in Table 1 appears to meet this criterion.

To assess compatibility of polymer blends, dynamic mechanical analysis (DMA) was performed to obtain Tg data of components and blends. A single Tg of the polymer blend and adherence to the Fox equation can provide evidence of miscibility.

The Fox equation (Eq. 1) was used to determine the theoretical Tg's of the polymer blend and tackified polymer blend. The minimal differences between the theoretical and experimental Tg's (Table 2) show adherence to the Fox equation and indicates miscibility of the hybrid blends.

Equation 1. Fox Equation[5]

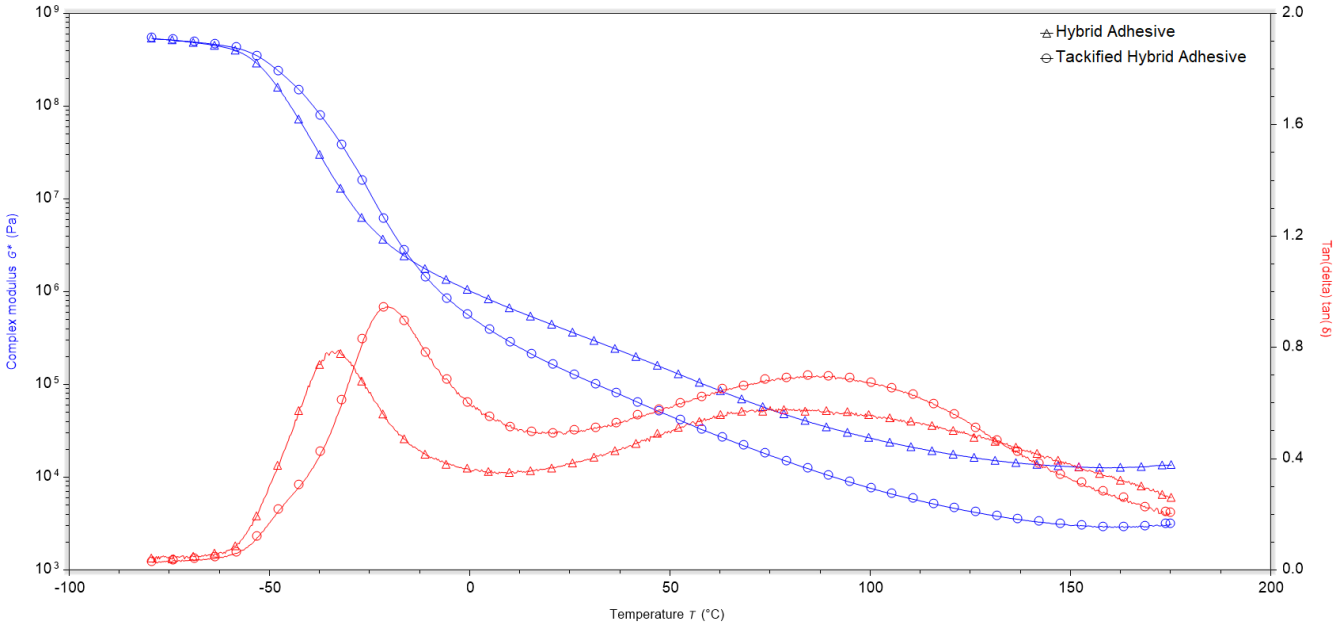
$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} + \ldots$$

Table 2. Tg Calculation Results

Mixture	**Theoretical Tg (°C)**	**Experimental Tg (°C)**	**ΔTg (°C)** **(Experimental – Theoretical)**
Acrylic-Urethane Blend	-37	-33	4
Tackified Blend	-21	-21	0

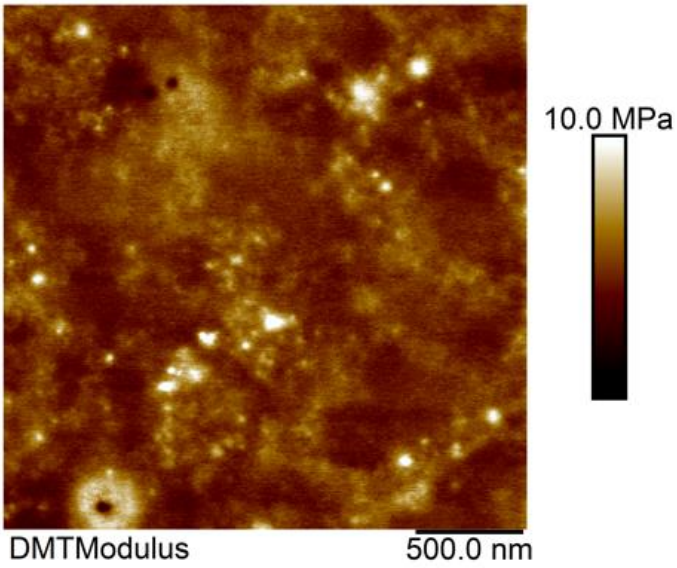
The single Tg of the polymer blend, as seen in the DMA Temperature Ramp (Figure 1), is further evidence of the miscibility of the acrylic and urethane polymers. The single Tg of the tackified blend showcases the compatibility of the rosin ester tackifier with the hybrid blend.[6]

Figure 1. Temperature Ramp of Polymer Blends



To further evaluate the miscibility of the acrylic-urethane blend, atomic force microscopy (AFM) images were obtained. The scale bar for the modulus channel shows that lighter areas have a higher modulus while darker areas have a lower modulus. It is evident that the lower modulus continuous phase is composed of urethane soft block and acrylic polymer, while the higher modulus areas indicate urethane hard blocks (Figure 2).

Figure 2. AFM of Acrylic-Urethane Blend



Test Methods

Viscosity

Viscosity was measured using a Brookfield Viscometer with spindle LV-62.

Atomic Force Microscopy

Samples were analyzed with a Bruker Dimension Icon AFM in Peak Force Tapping mode. An RTESPA-150 probe was used with a 7.5nN setpoint. Images were collected at 5um and 2.5um.

Rheology – Temperature Ramp

A 3°C/min oscillation temperature ramp was run on a DHR-2 rheometer with 8mm parallel plates at a constant strain of 0.05% and frequency of 1 Hz.

Mixing Procedure

The adhesives were mixed using an overhead stirrer and propeller blade. For the hybrid adhesive, the base polymers were mixed for five minutes at 600 rpm, which creates a sufficient vortex. Then, the crosslinker was added and incorporated for an additional five minutes at 700 rpm. For the tackified hybrid adhesive, the base polymers and tackifier were mixed for five minutes at 600 rpm. Then, the crosslinker was added and incorporated for an additional five minutes at 700 rpm.

Coating / Laminating

Mayer rods were used to coat the adhesives on foil and olefin substrates. The coatings were dried in a 75°C oven for two minutes. The coat weight was 4-6 lb/ream (~8 gsm). The coatings on 1mil foil were laminated to the Corona-treated side of clear, 1 mil polyester, and the olefin coatings were laminated to another olefin substrate. The ChemInstruments hot steel roll laminator was used with settings of 275°F, 300 in/min, and 90 psi. The adhesive coated substrate was against the steel roll and the second substrate was against the rubber roll, mimicking the production process.

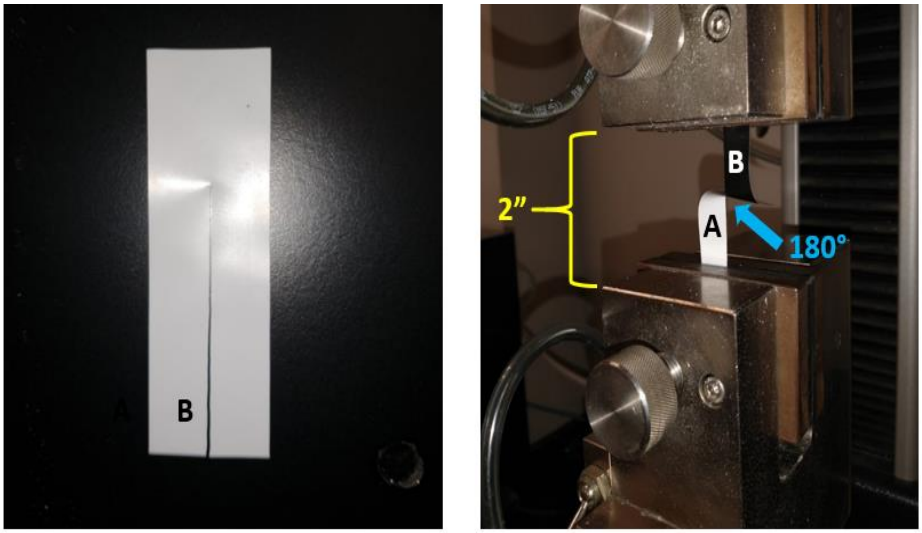
T-Peel for Foil/PET Laminates: ASTM D1876-08

To determine the peel force of the adhesive bonds between the foil and polyester substrates, ASTM D1876-08 was followed at a 3 in/min test speed using a 180° angle. The peel adhesion was recorded in lbf/in. The bond was tested in the green state, which is immediately after lamination. This test was repeated after the sample cured at ambient temperature for 24 hours and in the fully cured state, after 72 hours. Water resistance testing was also performed. The specimens were placed in a 75°C water bath for 15 minutes, removed and patted dry, before the T-peel test was repeated. The specimens were placed back in the 75°C water bath for an additional 24hrs, removed and patted dry, and the test was repeated for a final time. The failure modes were recorded (AF = adhesive failure, CF = cohesive failure).

Trouser Tear for Olefin Laminates: ASTM D1938-19

To determine the force necessary to propagate a tear in the laminate, the specimen was clamped in an Instron. ASTM D1938-19 was followed using a grip separation of 2 inches, a 10 in/min test speed, and a 180° angle, as shown in Figure 3.

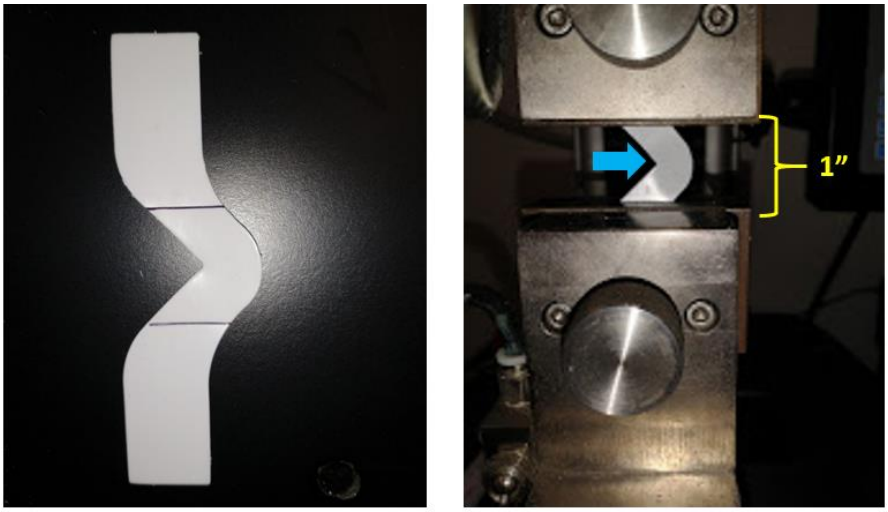
Figure 3. Trouser Tear



Graves Tear for Olefin Laminates: ASTM 1004-13

To determine the tear resistance of the laminate, the specimen was clamped in an Instron. ASTM 1004-13 was followed using a grip separation of 1 inch and a 2 in/min test speed, as shown in Figure 4.

Figure 4. Graves Tear



Puncture for Olefin Laminates: ASTM D1000-10

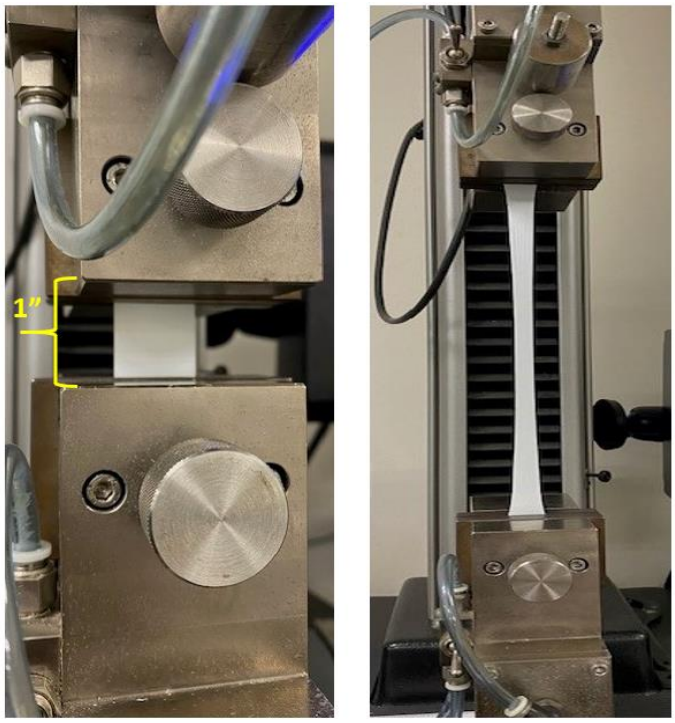
To determine the puncture resistance of the laminate, the specimen was clamped between two steel plates and a rounded probe descended to pierce a hole. ASTM D1000-10 was followed at a 2 in/min test speed, as shown in Figure 5.

Figure 5. Puncture

Tensile/Elongation for Olefin Laminates: ASTM D882

To determine the laminate’s breaking strength and elongation at break, a 1-inch-wide specimen was clamped in an Instron. A grip separation of 1 inch and a 20 in/min test speed was used, as shown in Figure 6.

Figure 6. Tensile/Elongation



Environmental Resistance: ASTM G154

To assess the environmental resistance of laminates that utilize both hybrid adhesives, ASTM G154 was followed. The laminates were conditioned in a QUV Accelerated Weathering Tester with UVA-340+ lamps set to an irradiance of 0.89 W/(m^2•nm). The exposure cycle involved 8 hours of UV exposure at 60°C followed by 4 hours of condensation at 50°C, repeated for 7000 hours.

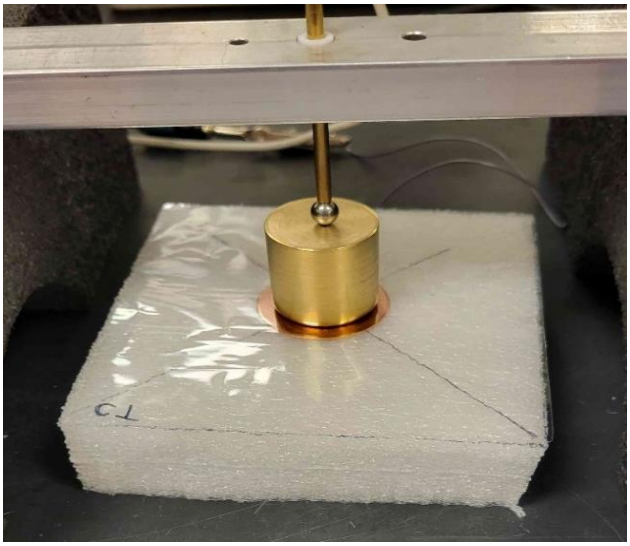
Fluid Resistance for Olefin Laminates: GMW16653

To determine the chemical resistance of the laminate, GMW16653 was followed. The specimen was dipped in four different automotive fluids and drained for 1 hour each. The automotive fluids used were motor oil, power steering fluid, transmission fluid, and brake fluid. To further evaluate the chemical resistance of the laminate, harsher conditions were followed compared to GMW16653. The specimen was soaked in the same four automotive fluids and monitored for delamination after 30 minutes, 1 hour, 1 day, and 1 week.

Dielectric Breakdown: ASTM D3755

To determine the dielectric breakdown voltage of the laminates, ASTM D3755 was performed using the following electrodes – a 1 inch diameter cylindrical brass rod (modified Type 2) on top and a 1¼ inch flat copper electrode on the bottom (Figure 7). The voltage was increased at a rate of 500 V/s until breakdown. The maximum voltage of the system was 30kV. Testing was performed at ambient temperature in air. The sample size was approximately 4 square inches and ten samples of each material were tested.

Figure 7. Dielectric Breakdown



180° Peel Adhesion for Olefin Laminates: PSTC-101

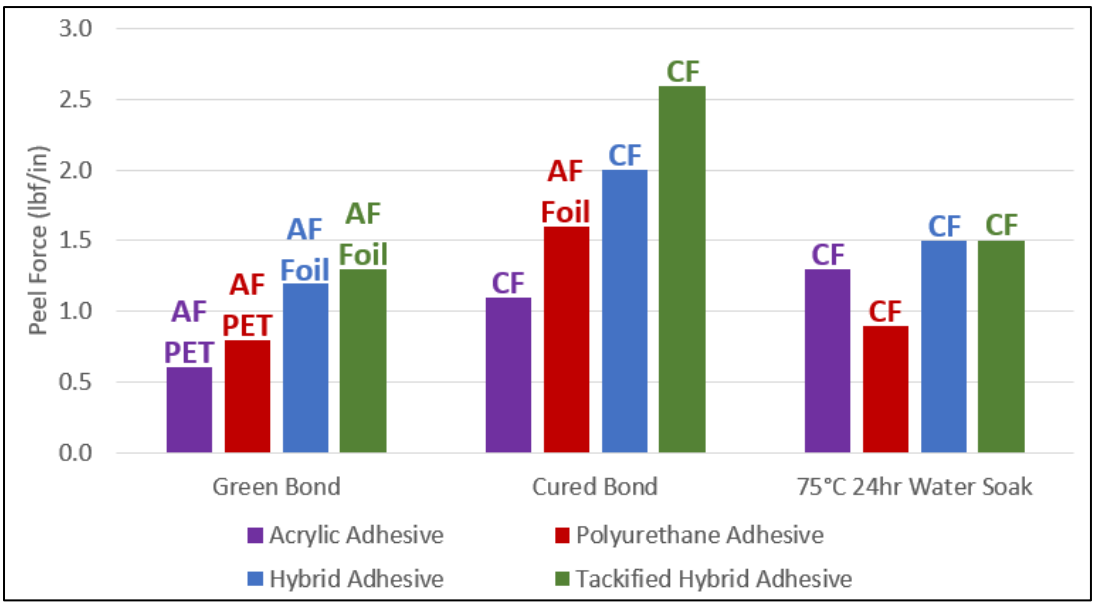
The olefin/olefin laminate is used as a layer in a multi-layer commercial product for exterior flashing and pipe ducts. To evaluate its utility as a tape backing, Method E of PSTC-101 was followed using type 304 stainless steel panels. The laminate was hand Corona-treated before applying 3M 467MP transfer tape (2.3 mil) and laminating with release liner at 150 in/min and 40psi. The laminate with transfer tape was left at ambient conditions overnight before proceeding. Peel strips were removed at 12 in/min after 20 minutes, 24 hour and 1 week dwell times.

Results & Discussion

Interlayer Adhesion and Water Resistance of Foil/PET Laminates

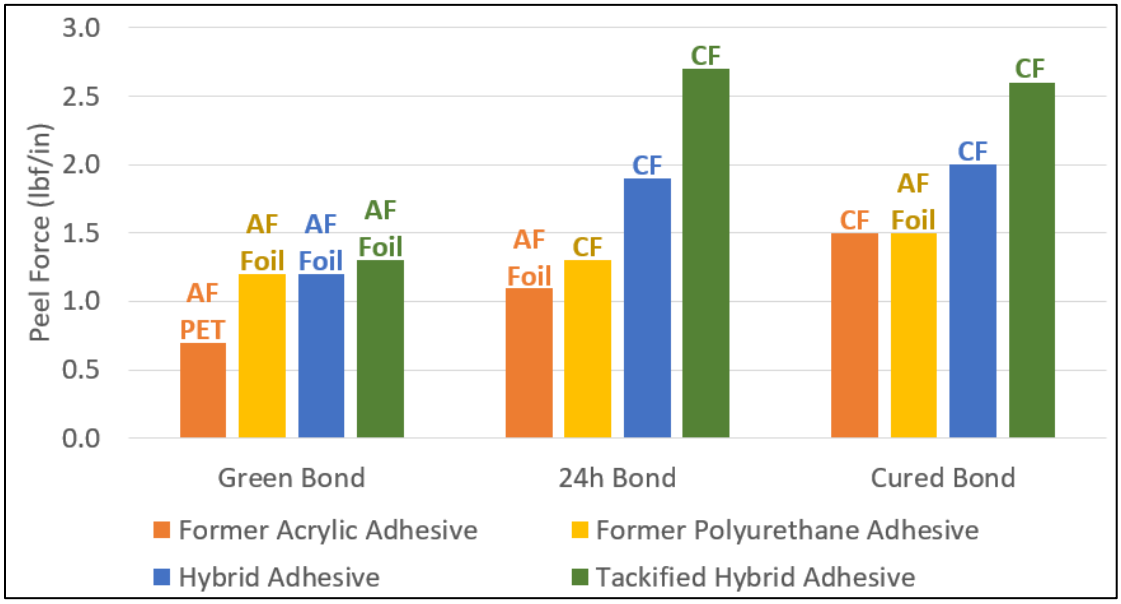
Foil/PET laminates are commonly used as component layers in exterior cladding, where environmental resistance is important. The untackified and tackified hybrid adhesives had superior performance compared to the individual base components in the T-Peel testing of the laminates, as shown in Figure 8. Coatings were 4-6 lb/ream (~5gsm). All formulations were crosslinked with isocyanate crosslinker. The green, cured, and 24hr water soak adhesion values were higher for the hybrid adhesives compared to the acrylic and polyurethane adhesives alone. The tackified hybrid adhesive had the highest cured bond at over 2.5 lbf/in without negatively impacting adhesion after water soak.

Figure 8. T-Peel Performance of Hybrid Adhesives vs. Individual Components



The T-Peel performance of two former workhorse waterborne adhesives is compared to the untackified and tackified hybrid adhesives on Foil/PET constructions at 4-6 lb/ream, as shown in Figure 9. The cured adhesion of the untackified and tackified hybrid adhesives are 30% and 70% greater than both former workhorse adhesives, respectively.

Figure 9. T-Peel Performance of Hybrid Adhesives vs. Former Workhorse Adhesives



Utility of Olefin Laminates as Tape Backings

Tear, Puncture, Tensile, and Elongation

The tear, puncture, tensile, and elongation at break performance of the olefin/olefin laminate, bonded with the untackified hybrid adhesive, was compared to the competitor's strength laminate. Results are shown in Table 3. The olefin/olefin laminate had similar tear and puncture values and 30% lower tensile strength at break, but 2.5x the elongation at break versus the competitive sample.

Table 3. Physical Properties of Olefin/Olefin Laminate vs. Competitor

Test	Olefin/Olefin Laminate	Competitive Laminate
Trouser Tear	5.0 lbf	5.4 lbf
Graves Tear	6.7 lbf	6.7 lbf
Puncture	9.3 lbf	10.1 lbf
Tensile at Break	24.6 lbf/in	37.1 lbf/in
Elongation at Break	960%	380%

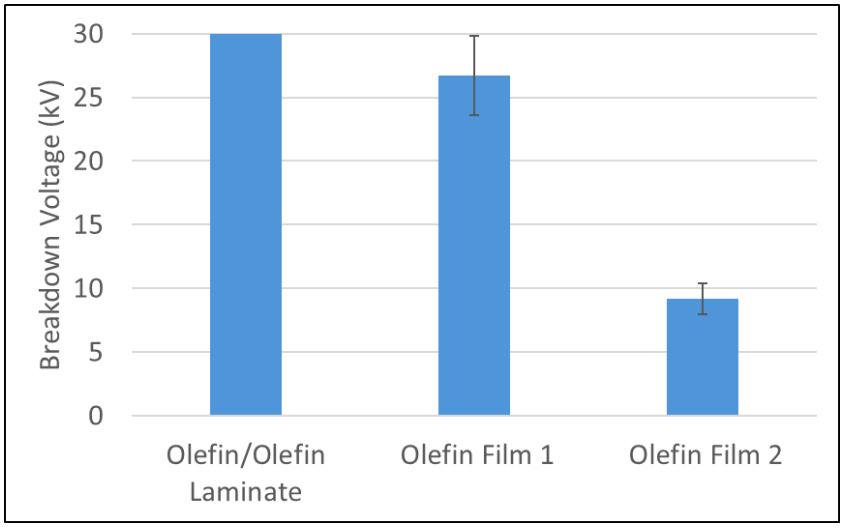
Environmental & Fluid Resistance

Multilayer laminates using both hybrid adhesives survived 7000 hours of UV/Condensation cycling. No delamination or tunneling was seen in the adhesive layers of the laminates, indicating excellent environmental resistance. The olefin laminate passed the fluid resistance testing (GMW16653 and the harsher conditions) for all four automotive fluids. No delamination or degradation of the laminate was seen after one week of exposure.

Dielectric Breakdown

Dielectric breakdown occurs when a material loses the ability to resist an electrical current. The dielectric breakdown voltage is the voltage at which the material fails and is no longer electrically insulating. High dielectric strength is required for applications such as electrical tapes and for EV battery applications. The olefin/olefin laminate, along with each of the films comprising it, was evaluated for direct current dielectric breakdown (Figure 10). The laminate did not experience breakdown and therefore had a breakdown voltage >30 kV. Olefin film 1 had an average breakdown voltage of 26.7 kV, not including two samples that exceeded 30 kV. Olefin film 2 had an average breakdown voltage of 9.2 kV. For comparison, the breakdown voltage of 1.4mil PET using this test method was 15 kV.

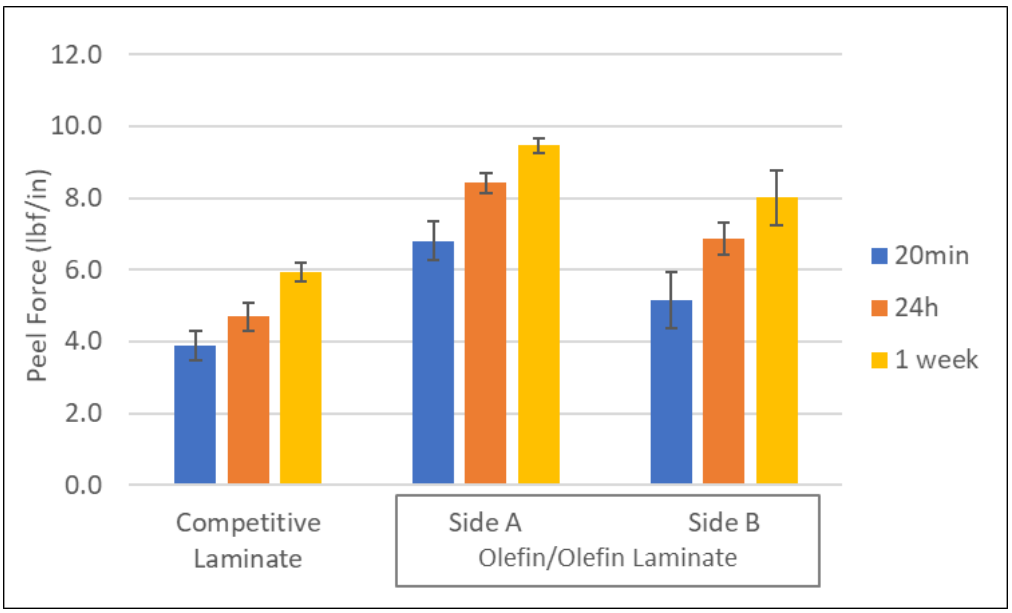
Figure 10. Dielectric Breakdown



180° Peel Adhesion to Stainless Steel Substrate

Single-ply olefin films are commonly used as tape backings. High performance applications, such as flashing tapes, require multiple layers of film with different attributes to achieve the required high elongation, tensile strength, puncture and tear resistance. Each side of the olefin/olefin laminate, bonded with the untackified hybrid adhesive, and a competitive strength laminate was backed with a commercially available transfer tape and evaluated according to PSTC-101 off stainless steel. Results are shown in Figure 11. Peel adhesion was tested after 20 minutes, 24 hours, and 1 week dwell at ambient conditions. Peel force was slightly different depending on which side of the laminate was bonded to the panel but both sides had higher adhesion than the competitive strength laminate. All peels were adhesive failure to stainless steel with no delamination, indicating that the bond between olefin films can withstand a 9 lbf/in peel force.

Figure 11. 180° Peel Performance of Olefin/Olefin Laminates vs. Competitive Strength Laminate



Applications

In addition to flashing and electrical tapes, laminates made with the hybrid adhesive are suitable for many applications within the building and construction and automotive markets.

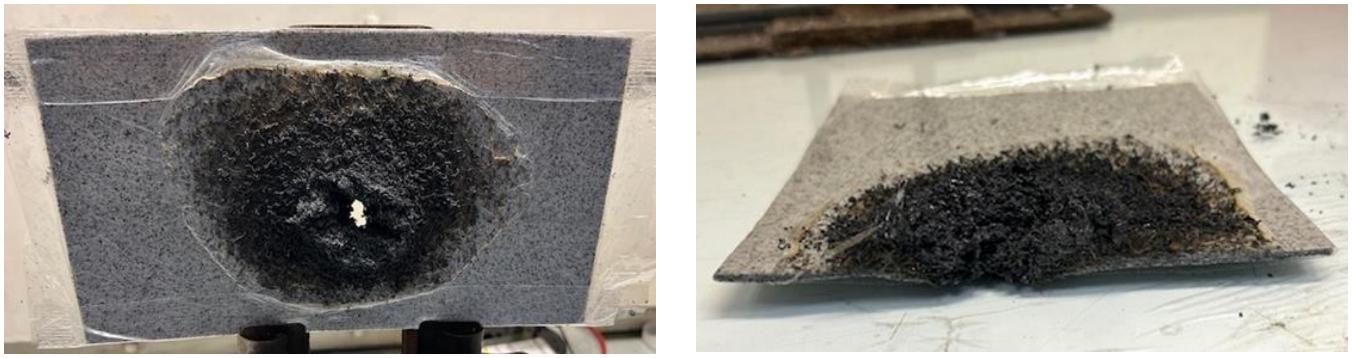
- The ability of the adhesive to bond dissimilar materials while maintaining good bond strength, superior environmental and fluid resistance and high breakdown strength make it a good candidate for wire harness tapes.
- Laminates comprised of ethylene vinyl alcohol films (EVOH), which provide good gas and water vapor barrier properties, and metallized PET can be made with the hybrid adhesive. These laminates are used in the production of vacuum insulation panels for use in appliances where a low profile is valued.
- Another area where this adhesive can be used is to construct a laminate for flexible gas line wrap, containing foil, PET and heat-activated engineered film. This high strength laminate provides lightning strike protection and is able to be sealed around the gas line.

Next Generation Flame Retardant Laminates

Expandable Nonwoven

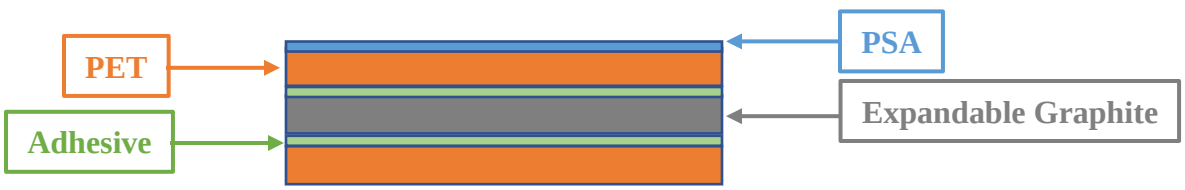
The hybrid adhesive can be used to create laminates with expandable glass nonwoven containing embedded intumescent graphite. The expandable nonwoven can provide fire protection in building and construction applications such as commercial buildings, doors, and roofing underlayments. The T-Peel of an expandable nonwoven/PET laminate was destructive, meaning the adhesive had higher cohesive strength than the nonwoven. To test the insulative properties of the expandable nonwoven, direct flame impingement was performed by exposing the laminate to a torch. Figure 12 shows how the expansion of the nonwoven creates a thick insulating char layer which prevents further flame spread.

Figure 12. Expandable Nonwoven/PET Laminate After Torch Exposure



PSA can be applied to the outer layer of a PET/expandable nonwoven laminate (Figure 13) for tape backing applications such as EV battery assemblies and roofing underlayment.

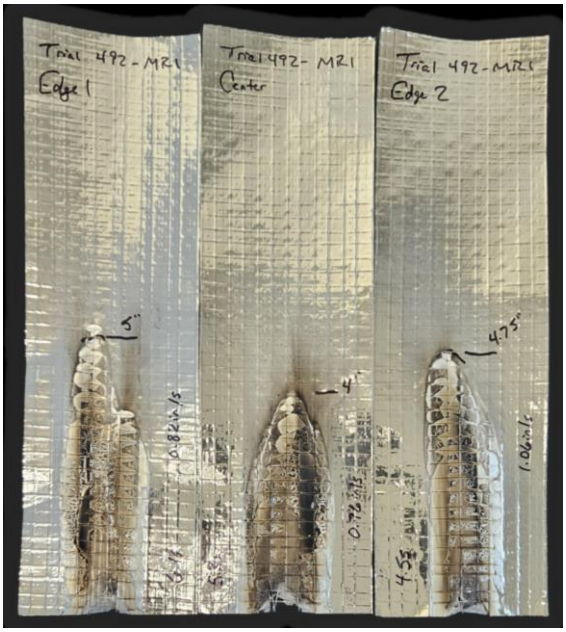
Figure 13. PSA/Expandable Graphite Laminate Construction



Non-Halogenated Facing Tape Backing

The hybrid adhesive can also be used as a base for non-halogenated adhesive formulations. As safety and environmental concerns of halogenated flame retardants (FRs) and heavy metals have grown, non-halogenated solutions have become even more important. The relatively low storage modulus of the hybrid adhesive allows the formulation to be heavily loaded with flame retardants while maintaining a good bond. An example of a laminate for facing tape contains PET, scrim and foil. Figure 14 shows passing results of a 10s vertical burn of a construction made with non-halogenated FR adhesive utilizing the hybrid adhesive.

Figure 14. PET/Scrim/Foil Laminate



Conclusions

The miscible acrylic-urethane hybrid adhesives explored in this paper can be used to create durable industrial laminates with unique performance attributes.

- PET/foil laminates exhibit superior bond strength compared to adhesives based on acrylic or urethane alone and can be utilized for exterior applications in building and construction markets.
- Olefin/olefin laminates made with the hybrid adhesive have excellent tensile, puncture, tear and elongation properties. These laminates also have exceptional environmental and fluid resistance and high dielectric breakdown strength, making them suitable for various types of tape backings including electrical, wire harness or in EV battery applications.
- The hybrid adhesive's ability to create robust bonds between dissimilar materials can be capitalized upon to laminate unique materials such as EVOH or expandable glass nonwoven, which can further provide barrier and flame retardant properties respectively.

References

1. Straits Research, “Water-Based Adhesive Market Size, Scope, Growth Report 2033”, https://straitsresearch.com/report/water-based-adhesive-market, 2024.
2. Zhang, J., et al. Dow Global Technologies LLC. Process for Preparing Polyurethane/Acrylic Hybrid Dispersions. WO2013091211A1. Shanghai Patent & Trademark Office, LLC. June 27, 2013.
3. Galgoci, E.C., Hegedus, C.R., Snyder, J.M., Lawson, III, D.C., Lindenmuth, D.L., “Urethane-Acrylic Hybrid Polymers: Performance as 1K Coatings”, Air Products and Chemicals, Inc., The Society of the Plastics Industry/Epoxy Resin Formulators Division Conference, 2001.
4. Noshay, A., McGrath, J.E., Block Copolymers: Overview and Critical Survey, New York, NJ, Academic Press, Inc., 1977.
5. Sperling, L.H., Introduction to Physical Polymer Science, New York, NY, John Wiley & Sons, Inc., 2001.
6. Tobing, S.D., Klein, A. (2000). Mechanistic Studies in Tackified Acrylic Emulsion Pressure Sensitive Adhesives. *Journal of Applied Polymer Science*, Vol. 76, 1965-1976.

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