IMPROVED ADHESION OF SILICONE ROOF COATINGS TO DIFFICULT MEMBRANES WITH NOVEL SILANES

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The mounting pressure to reduce VOC emissions in industrial coating systems has led to increased demand and new developments of high-solids coatings within the cool-roof market. These coatings allow for greater solar reflectance, keeping residential and commercial buildings from overheating. Organofunctional alkoxysilanes are widely used additives in industrial coatings as they form a bridge between organic coatings and inorganic substrates. While most alkoxysilane monomers liberate VOCs in the range of 450–600 g/L, new alkoxysilane oligomers offer even better adhesion properties for coatings while emitting lower VOCs (<350 g/L). This work will demonstrate the significant improvement to adhesion for difficult roofing membranes such as ethylene propylene diene monomer (EPDM), polyvinylidene fluoride (PVDF), and spray polyurethane foam (SPF), and to mechanical properties of high-solids alkoxy-cured silicone roof coatings with the addition of low-VOC silane oligomers. As the market for these coatings continues to grow, alkoxysilane additives will play an important role in achieving better performance and increasing their longevity.

Introduction

The cool-roof market has been rapidly expanding alongside advancements in sustainable roof coatings technology. In addition to functionally cool roofs that provide greater solar reflectance, these roof coatings need to maintain low volatile organic compounds (VOCs) and excellent performance properties. Although the current market utilizes oxime-cured silicone roof coatings, high-solids alkoxy-cured silicone roof coatings can provide equally good performance while eliminating toxic methyl ethyl ketoxime as a byproduct. The work covered in this article will demonstrate that with the use of organofunctional silane additives, several crucial performance characteristics of alkoxy-cured silicone roof coatings can be improved.

The mechanism behind an organofunctional silane adhering to a roofing membrane surface is an important process to understand. Organofunctional silanes contain an alkoxy functional group (Si-OR) that can be hydrolyzed to bond with inorganic surfaces and an organofunctional group that can react with organic systems such as silicone resins. The reactions of the alkoxy functional groups and organofunctional groups allow these silanes to act as an adhesion promoter between inorganic and organic materials. These reactions are moisture driven and the alkoxy sites must first undergo hydrolysis to form silanol groups. The silanol groups then react with the hydroxyl groups on the inorganic surface of the roofing membrane to create siloxane bonds, which provide strong adhesion properties **(Figure 1)**. As well as bonding with the substrate's inorganic surface, the silanol groups can self-condense to create additional siloxane bonds, increasing crosslink density and improving mechanical properties of the coating **(Figure 2)**.

Several key coating properties will be investigated in accordance with ASTM D6694, the standard for liquid-applied silicone roof coatings used by roofing manufacturers and contractors. These properties include surface hydrophobicity, water-ponding resistance, elongation, tensile strength, and dry and wet adhesion to various roofing membranes.

Experimental Methods

Coating Systems and Materials

The work investigated in this article consists of three coating systems, all of which were identical except for the presence and choice of silane additive. The control system, referred to as "control," did not contain any silane. One experimental system contained a "specialty aminoalkylsilane oligomer." The second experimental system contained a "specialty aminosilane blend." The remaining materials used in this work can be found in **Table 1**.

EPDM and PVDF roofing membranes were purchased from McMaster-Carr. SPF panels were created for the purpose of this testing and formulated using new hydrofluoroolefin blowing agents (HFO), which are now replacing hydrofluorocarbon blowing agents (HFC) in SPFs. Aluminum wire mesh 304 grade with 28 openings per inch was also purchased from McMaster-Carr.

Formulation Preparation

The two silicone resins were mixed before carefully adding in the calcium carbonate. The moisture scavenger and plasticizer were mixed in, followed by the fumed silica. The emulsifier was ground into a fine powder using a mortar and pestle and then added to the formulation. The catalyst and specialty silane were added last. After each addition, the formulation was mixed at least three times using a FlackTek SpeedMixer for 1 minute at 1500 rpm.

Roofing Membrane Substrate Preparation

Two of the roofing membranes evaluated in this work, EPDM and PVDF, were purchased in their ready-to-use solid form. Before applying the silicone roof coatings onto the EPDM and PVDF roofing membrane substrates, these substrates were first aged in a QUV accelerated-weathering instrument for 350 hours. The QUV was carried out in accordance to ASTM G-154 with a UV light cycle for 6 hours at 60 °C followed by a condensation cycle for 4 hours at 50 °C. This process provided a more realistic aged roofing membrane surface that a high-solids alkoxy-cured silicone roof coating would be applied onto in the field. After aging, the membrane substrates were rinsed with water

FIGURE 1
Hydrolysis reaction of a silane molecule.

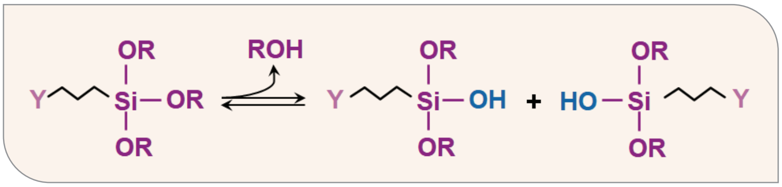


FIGURE 2
Condensation reaction of a silane molecule.

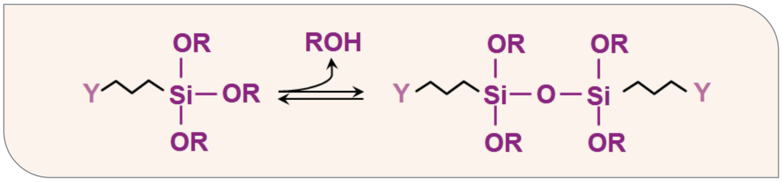


TABLE 1
High-Solids Alkoxy-Cured Silicone Roof Coating

Material	Supplier	Function	Weight (g)
BLUESIL FLD 48V 5000	Elkem Silicones	Silicone Resin	15.3
BLUESIL FLD 48V 750	Elkem Silicones	Silicone Resin	25.3
Hubercarb W325	Huber Engineering Materials	Calcium Carbonate Filler	47.0
Dynasylan® VTMO	Evonik	Moisture Scavenger	2.0
Vestinol® 9	Evonik	Plasticizer	5.0
Aerosil® 200	Evonik	Fumed Silica Filler	3.0
Stearic Acid	Sigma Aldrich	Emulsifier	2.0
TD 18 (Dioctyl tin carboxylate)	Evonik	Catalyst	0.1
Silane[1]	Evonik	Adhesion Promoter	0.3
[1] VOC of specialty aminoalkylsilane oligomer = ~300 g/L and specialty aminosilane blend = ~540 g/L		**Total**	**100.0**

and dried with compressed air before applying the roof coatings. The SPF roofing membrane was not aged, but a planar was used to create a flat surface.

Cure Schedule

The coatings were applied onto the aged roofing substrates by pouring on the coatings and leveling out to the desired film thickness using a trowel. Then, the coatings were cured at ambient temperature (23 °C) and constant humidity (40% relative humidity) for a minimum of 14 days before any test methods were performed.

Test Methods

Contact-Angle Measurement

Once the coatings were fully cured, a ramé-hart goniometer was used to measure the contact angle of deionized water on the coated substrate surfaces. Each measurement reported in this article was the average of 10 contact-angle measurements to ensure the accuracy of the method.

Water-Ponding Resistance

As derived from ASTM D471, free films of the alkoxy-cured silicone roof coatings were created and cured for a minimum of 14 days at 23 °C and 40% humidity. The coating sample was then immersed in room temperature deionized water for seven days (168 hours). After this immersion period, the film was taken out of the deionized water bath, dried off with air, and weighed again. After the water immersion, the percentage difference in weight was calculated.

Elongation at Break Measurement

As derived from ASTM D2370, the alkoxy-cured silicone roof coatings were poured into a Teflon mold (length: 150 mm; width: 60mm; depth: 5 mm) and allowed to cure for a minimum of 14 days at 23 °C and 40% humidity. These cured free films were cut into “dogbones” (an elongated bone or barbell shape) and evaluated on a Tinius Olsen tensile-testing instrument for elongation at break. This measurement is the calculation of the percent change in length at breakage when strained at a constant rate.

Tensile-Strength Measurement

As derived from ASTM D2370, the alkoxy-cured silicone roof coatings were poured into a Teflon mold (length: 150 mm; width: 60 mm; depth: 5 mm) and allowed to cure for a minimum of 14 days at 23 °C and 40% humidity. These cured free films were cut into dogbones and evaluated on a Tinius Olsen instrument for tensile strength. This measurement is the calculation of the maximum pull strength on the Tinius Olsen instrument in units of MPa when strained at a constant rate until break.

Dry-Adhesion Testing

As derived from ASTM C794, an aluminum wire mesh was embedded in between two 10 mil dry film thickness coatings on each roofing membrane substrate. The coating was allowed to cure for a minimum of 14 days at 23 °C and 40% humidity before placing the sample in a Tinius Olsen tension testing machine. The aluminum wire mesh was peeled back from the substrate at a 180° angle, and the force required to peel back the aluminum wire mesh from the roofing membrane substrate was measured in pli. The mode of failure was also observed and reported, i.e., adhesive failure, cohesive failure, or mixed failure. Adhesive failure was defined as a loss of adhesion at the substrate-coating interface while cohesive failure was defined as a failure within the coating itself; mixed failure was when both adhesive and cohesive failure were observed.

Wet-Adhesion Testing

The wet-adhesion testing procedure was identical to the previous dry-adhesion testing procedure with the exception that the wet-adhesion measurements were taken immediately after the cured-coating system had been immersed in deionized water for an additional seven days.

Results and Discussion

Contact Angle

The surface hydrophobicity of the coatings was measured by observing the contact angle of deionized water on the coating surface. The addition of a silane to the formulation provided a notable improvement to the hydrophobicity of the coating, increasing the contact angle by more than 50%.

This increase in hydrophobicity can be explained by the presence of alkyl groups in the specialty aminoalkylsilane oligomer. The specialty aminosilane blend also contains more alkoxy groups which increased the number of siloxane bonds, improving crosslinking density and preventing water seepage. **Figure 3** shows the contact angle of each coating system.

Water-Ponding Resistance

Water uptake resistance was measured for these coatings, and the weight of water

FIGURE 3
Contact angle of deionized water on cured free film.

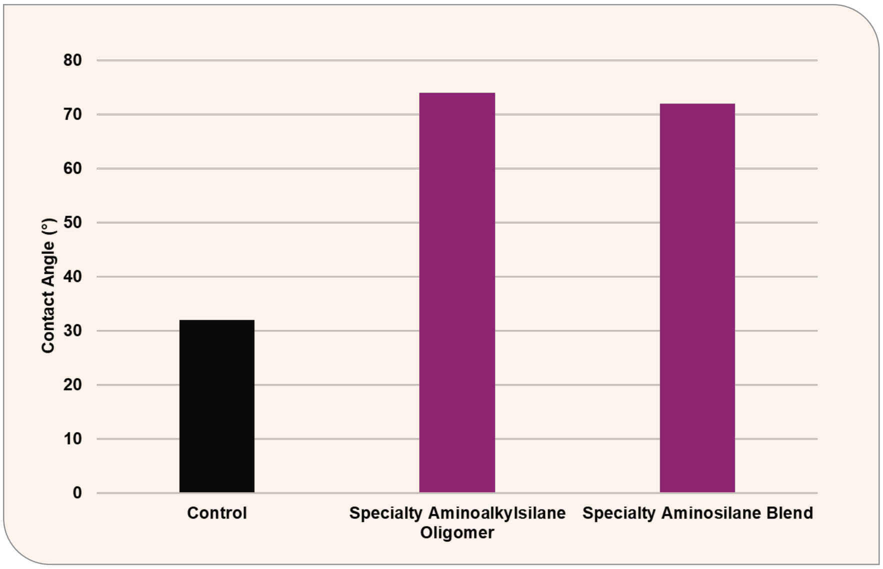


FIGURE 4
Percentage of water absorption of cured free film after one week submersion in deionized water.

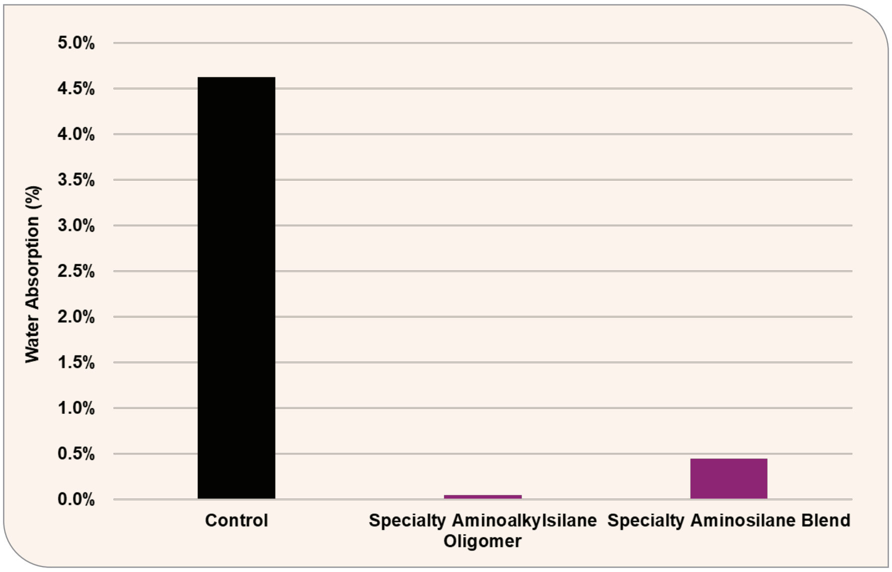


FIGURE 5
Shore hardness of cured free films.

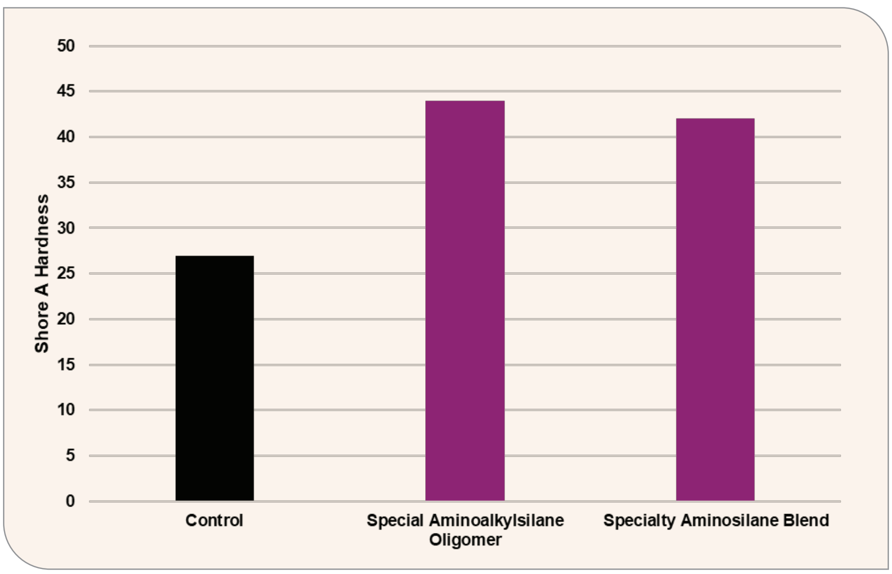
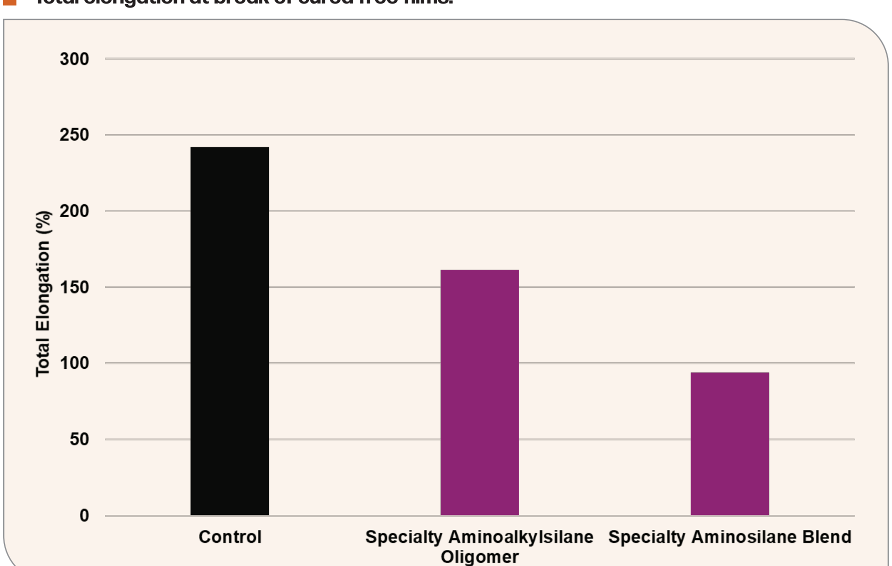


FIGURE 6
Total elongation at break of cured free films.



absorbed was calculated. The control coating absorbed distinctly more water and had an absorption nearly 400% greater than that of the silane-containing coatings.

Although silicone roof coatings are naturally hydrophobic, water-ponding resistance is still crucial for commercial applications as large volumes of sitting water can prematurely age the coatings and the substrates beneath them. The addition of a silane increases the crosslink density of the coating, resulting in a more durable and water-repellant coating. **Figure 4** shows the water-ponding resistance of each coating system.

Elongation at Break

The elongation at break properties of the coatings with and without silane additives were investigated on cured free films. This mechanical property is significant for the roofing market as these coatings undergo constant expansion and contraction due to the surrounding environment. The silane-containing coatings demonstrated a decrease in elongation when compared to the control. However, this outcome is likely a result of increased crosslinking due to the silane additive. The control coating was likely under cured and therefore exhibited relatively better elongation as the coating was soft and flexible. **Figure 5** shows the Shore A hardness of each coating system (ASTM D2240).

According to ASTM D2370, the minimum requirement is 100% elongation so despite having slightly less total elongation than the control, the specialty aminoalkylsilane oligomer surpasses this requirement and the specialty aminosilane blend meets it. **Figure 6** shows the total elongation at break of each coating system.

Tensile Strength

The improved crosslinking density from the silanes can lead to increased toughness and durability of the coating which can be measured and correlated with the tensile strength of the system. With the addition of either silane, the tensile strength of the coating increased by more than 300%, indicating increased crosslink density due to the presence of alkoxy functional groups. **Figure 7** shows the tensile strength of each coating system.

Dry and Wet Adhesion on Aged EPDM

The dry- and wet-adhesion properties of the coatings were investigated on aged EPDM. The force required to pull the aluminum wire mesh out of the roof coatings on aged EPDM at a 180° angle was measured in pli.

For both dry and wet adhesion, adhesive failure was observed for all coatings samples tested. Although there was no impact to dry adhesion from the addition of a silane, the presence of either silane significantly improved the wet adhesion to EPDM by at least 250%. The improved wet-adhesion result could be due to increased crosslinking of the coating in the presence of excessive moisture, giving the coating more resistance during the 180° angle pull. Under these conditions, there was more water available to promote hydrolysis and increase the siloxane bonds created in the coating, improving the coating's adhesion to the substrate.

ASTM C794, the standard for wet adhesion, states that the minimum force requirement for wet adhesion is 2pli, so without the use of a silane, the control coating would fail by this standard. Given the outdoor application of these roof coatings, wet adhesion provides a more realistic simulation of cure conditions whereas dry adhesion occurs in an idealistic environment. **Figure 8** shows the dry and wet adhesion of each coating system on aged EPDM.

Dry and Wet Adhesion on Aged PVDF

The dry- and wet-adhesion properties of the coatings were investigated on aged PVDF. The force required to pull the aluminum wire mesh out of the roof coatings on aged PVDF at a 180° angle was measured in pli.

For both dry and wet adhesion, adhesive failure was observed for all coatings samples tested. The addition of the specialty aminosilane blend provided improved dry adhesion over the control by 100%, and the presence of either silane significantly improved the wet adhesion to PVDF by at least 300%. Similar to the adhesion results on aged EPDM, the improved wet adhesion result was likely due to increased crosslinking of the coating in the presence of excessive moisture, giving the coating more resistance during the 180° angle pull.

FIGURE 7
Tensile strength of cured free films.

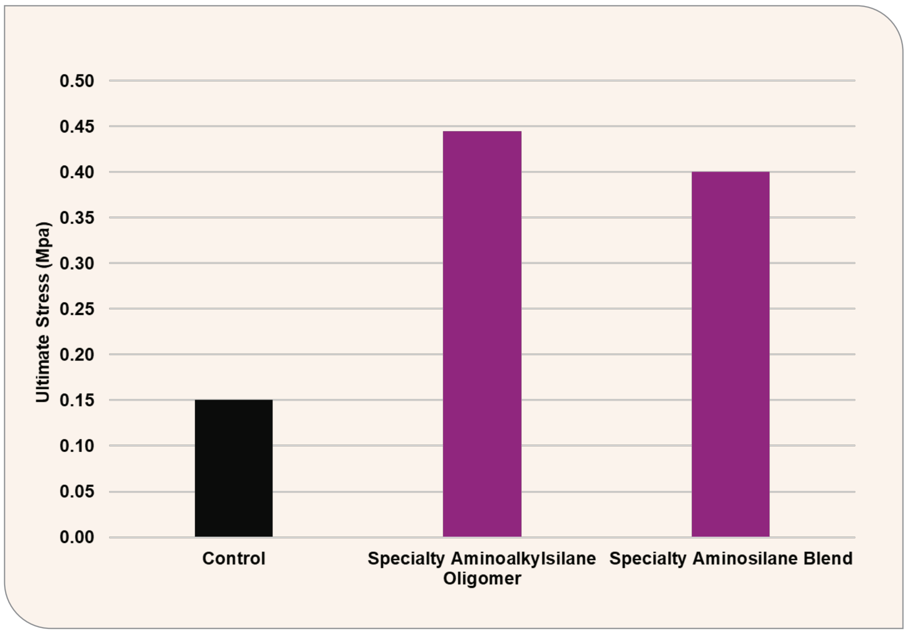


FIGURE 8
Dry- and wet-adhesion values of silicone roof coatings on aged EPDM.

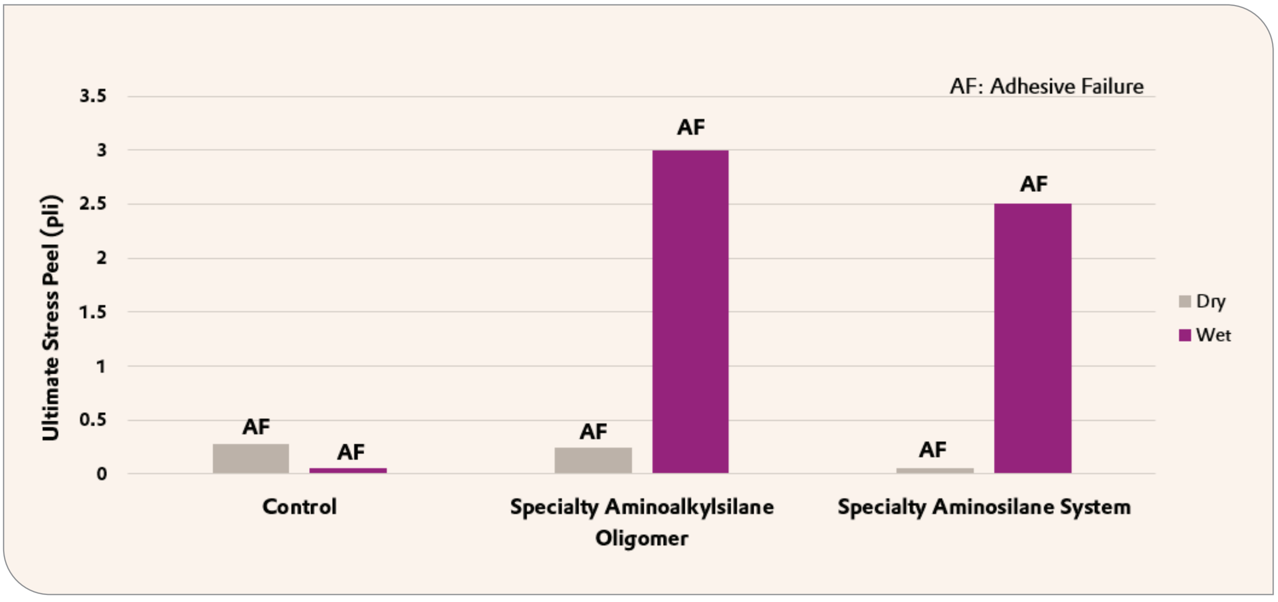


FIGURE 9
Dry- and wet-adhesion values of silicone roof coatings on aged PVDF.

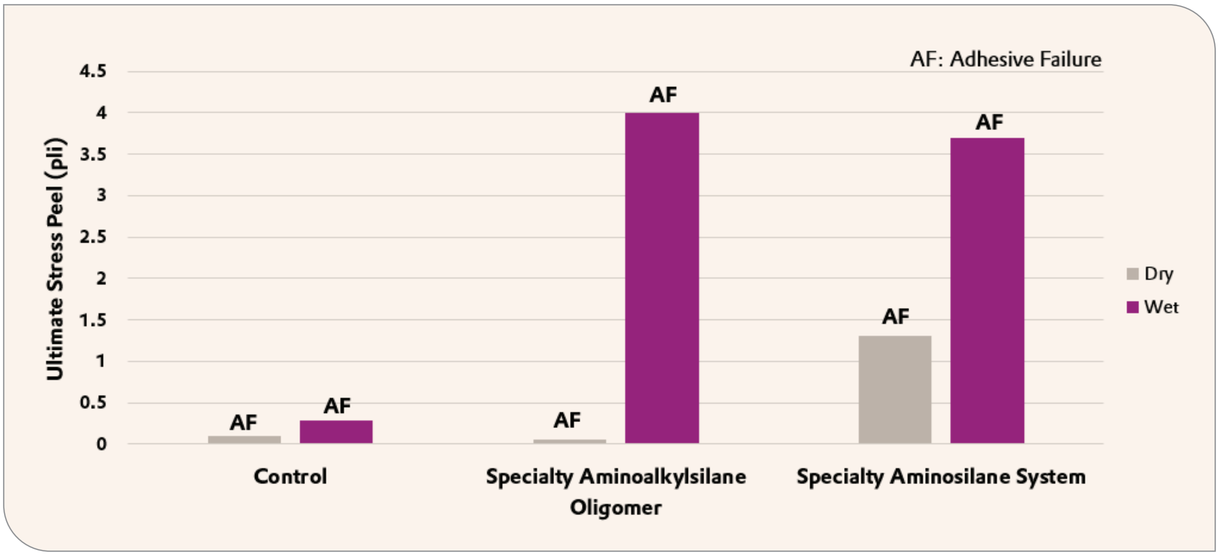


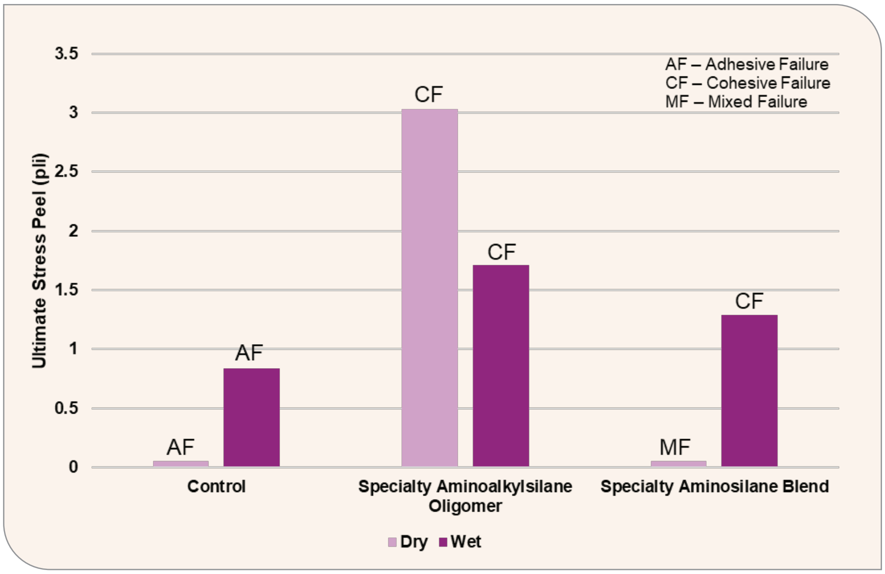
Figure 9 shows the dry and wet adhesion of each coating system on aged PVDF.

Dry and Wet Adhesion on Spray Polyurethane Foam

The dry- and wet-adhesion properties of the coatings were investigated on SPF. The force required to pull the aluminum wire mesh out of the roof coatings on SPF at a 180° angle was measured in pli.

For both dry and wet adhesion, multiple failure modes were observed for all coatings samples tested. The addition of the specialty aminoalkylsilane oligomer improved dry adhesion over the control by 300%, and the presence of either silane improved the wet adhesion to SPF by at least 50%. What is most significant to note is that the use of a silane changed the mode of failure from adhesive failure to cohesive or mixed failure, indicating increased coating adhesion to the substrate. **Figure 10** shows the dry and wet adhesion of each coating system on SPF.

FIGURE 10
Dry- and wet-adhesion values of silicone roof coatings on SPF.



Conclusion

As the cool-roof market begins to move away from oxime-cured silicone roof coatings to alkoxy-cured silicone roof coatings, the work investigated in this article is as important as it is relevant. There are numerous sustainability benefits to switching to high-solids alkoxy-cured silicone roof coatings; formulating with oligomeric silanes over conventional monomeric types reduces VOC emissions because oligomers can emit at least 20% less VOCs. However, performance deficiencies have been observed with the current technology. The crosslinking improvements provided by the addition of a silane are crucial to closing the gap in performance and meeting the market expectation when converting from oxime-cured silicone roof coatings, especially in regard to improved hydrophobicity and substrate adhesion. As the SPF industry begins to shift away from HFC blowing agents to new, more environmentally friendly HFO blowing agents, maintaining substrate adhesion with this changing surface chemistry will be vital. As demonstrated by this work, the usage of silanes even at low loading levels is a relatively inexpensive method to sustainably improve performance properties of alkoxy-cured silicone roof coatings.

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