Advances in One-component PVDF-acrylic Hybrid Dispersion and Its Applications

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For many years, aqueous hybrid dispersions of poly(vinylidene fluoride) (PVDF) and acrylic resins have been formulated into waterborne topcoats because of their exceptional weatherability and ability to meet stringent volatile organic compound (VOC) requirements and sustainability targets. For applications requiring strong chemical resistance, hydroxy-functional PVDF-acrylic dispersions are available which allow formulators to build resistance properties with isocyanate crosslinking. However, isocyanate not only presents respiratory hazards to paint applicators, but it can cause microfoaming in the resultant films due to CO_2 generation from the reaction of isocyanate with water. Recently, new one-component self-crosslinkable PVDF-acrylic hybrid latexes were successfully developed, and can be formulated
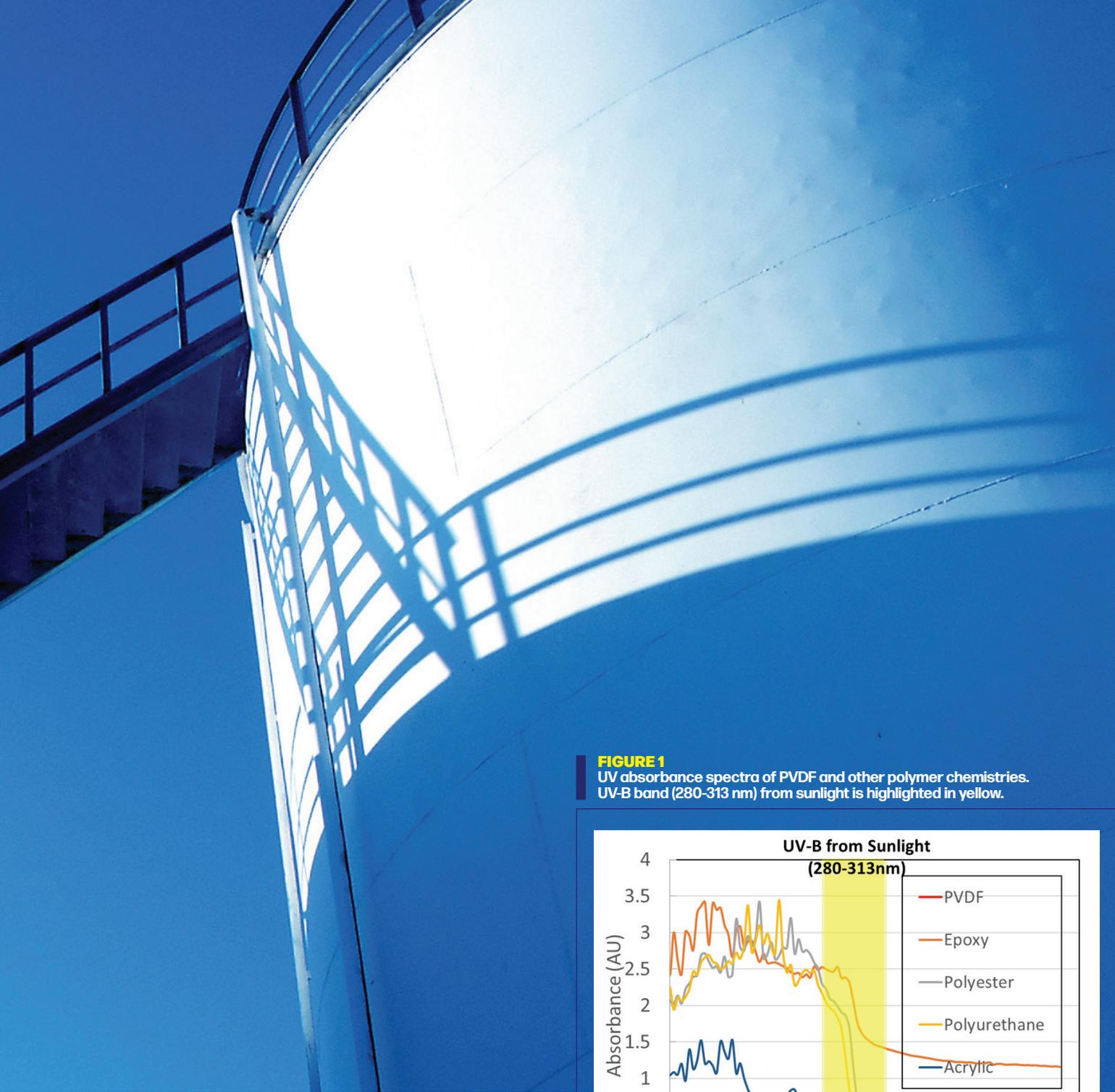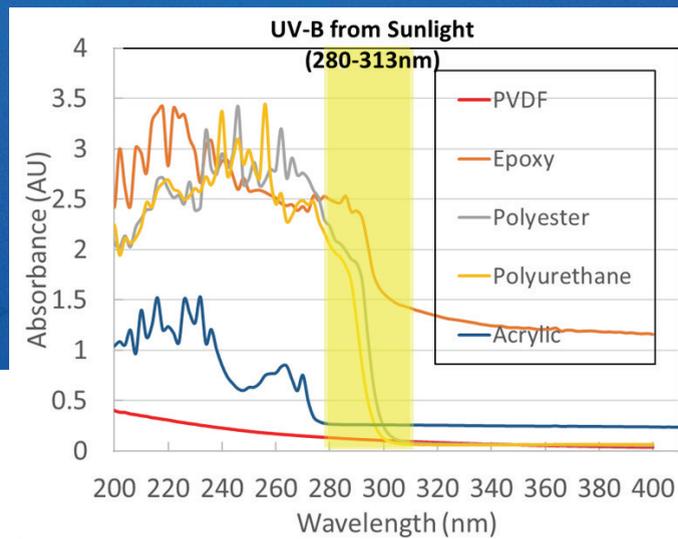
FIGURE 1
UV absorbance spectra of PVDF and other polymer chemistries. UV-B band (280-313 nm) from sunlight is highlighted in yellow.

below 100 g/L VOC. Detailed properties, such as detergent resistance, chemical resistance, and dirt pick-up resistance, in target applications such as architectural façade coatings and protective coatings are presented.

Introduction

Poly(vinylidene fluoride) (PVDF)-based topcoats[1] have been used for decades on monumental buildings around the world, and they have become the gold standard for decorative property durability and substrate protection. This performance is attributed to PVDF's outstanding UV and chemical resistance, and its good barrier properties against moisture and oxygen. The superior UV and chemical resistance of PVDF, relative to other common coating polymer chemistries, is demonstrated by its extremely low absorbance in the UV, as can be seen in **Figure 1**. The UV absorbance spectra were normalized to 25 µm dry film thickness. PVDF copolymer with hexafluoropropylene (HFP) comonomer was used in this study.

PVDF-based coatings have historically been limited to factory-baked coatings on metal because of the need for a high-temperature bake (230-250 °C) to alloy the

FIGURE 2
Twenty years' South Florida field exposure weathering panels of one-component PVDF-acrylic-based waterborne coatings (as shown in left for each color) vs legacy solventborne baked PVDF-acrylic coatings (right for each color). Panels are exposed at 45° South-facing. The substrates of these panels are chromated aluminum Q-Panels (AL-412 from Q-Lab Corporation).
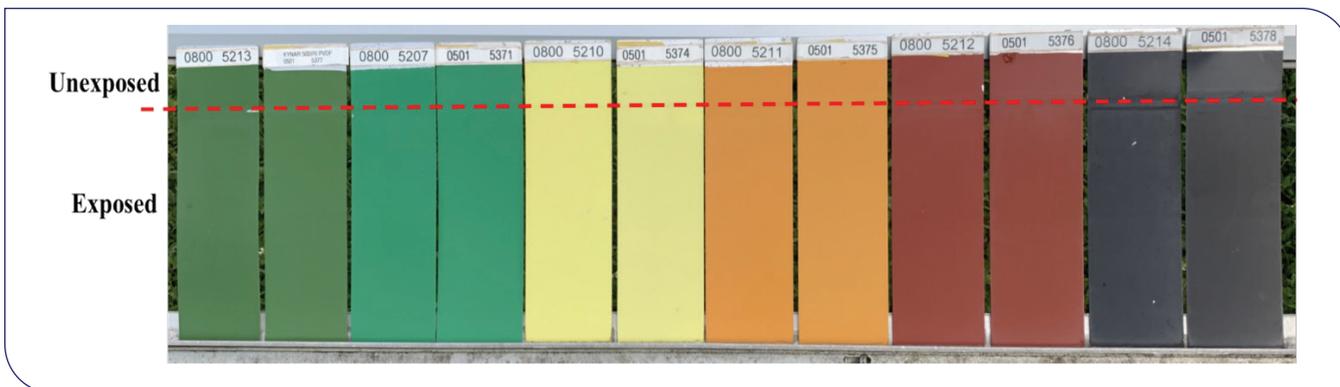
polymer components. These baked PVDF coatings, commonly used as topcoat finishes on monumental buildings and other architectural applications, typically contain a blend of 70-80 wt % PVDF resin with 20-30 wt % of a miscible acrylic resin. Around the year 2000, water-based hybrid resin technology became commercially available,[2] combining PVDF copolymers and acrylic resins in pre-alloyed form.[3] The new water-based technology allows for the application of durable PVDF-based coatings under field-applied and low-temperature bake OEM conditions, with dramatically lower levels of emitted volatile organic compounds (VOCs). **Figure 2** shows some South Florida weathering panels for a commercial waterborne PVDF-acrylic binder, after 20 years of exposure. Minimal visible differences can be noted between the unexposed and exposed areas of the panels.

More recently, hydroxyl-functional PVDF-acrylic hybrid products in this class were developed, which could be used with crosslinkers such as water-reducible polyisocyanates.[4,5] These systems show enhancements in certain key properties such as early hardness, barrier properties, solvent resistance, and adhesion, with performance contributions coming both from the entangled polymer network and from the network formed by crosslinking reactions.[6]

However, similar to other two-component systems with isocyanate crosslinking, isocyanate not only poses respiratory hazards and carcinogenic potential to paint applicators, but it can also cause microfoaming in the resultant films due to CO_2 generation from the reaction of isocyanate with water in the paints. This is particularly noticeable when applying paint with a brush or roller outdoors (**Figure 3**).

In this article, we present studies for developing a one-component self-crosslinkable PVDF-acrylic hybrid latex and waterborne formulations based on this hybrid latex for architectural façade coatings and protective coatings.

Experimental

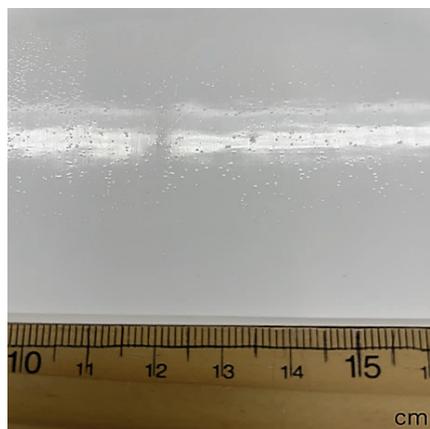### Synthesis of Self-crosslinkable PVDF-acrylic Hybrid Latex

A two-stage process was used to make the PVDF-acrylic hybrid latex.[7,8] PVDF latex was made in the first stage through emulsion polymerization of vinylidene difluoride monomer and an optional HFP comonomer in a pressure reactor. The second stage of the polymerization process, also called the acrylation stage, incorporated the acrylic monomers into PVDF latex to produce the intimate micromolecular mixture of PVDF and acrylic polymers. A wide variety of acrylic monomers with different T_g and functionalities can be chosen to tailor the coatings properties to the desired requirements. In this work,

FIGURE 3
Microfoaming issue with two-component waterborne paint with isocyanate crosslinking.

diacetone acrylamide (DAAM) monomer was introduced into the PVDF-acrylic hybrid latex along with other acrylic monomers and was copolymerized within the acrylic copolymers, creating well-dispersed pendant ketone crosslinking sites. Adipic dihydrazide (ADH) acted as a difunctional crosslinking agent, remaining partitioned in the water phase outside of the emulsion particles. ADH could be either added to the latex after emulsion polymerization was complete or during the paint formulation stage. Acrylic emulsions based on DAAM with ADH were initially nonreactive, ensuring emulsions maintained good long-term stability during shipping and storage. One-component keto-hydrazide self-crosslinking can occur at ambient temperature, facilitated by water evaporation during the film drying process and a simultaneous reduction in pH resulting from the loss of ammonia (a neutralization agent added in emulsion polymerization and paint formulation) (**Scheme 1**).

In this work, the characteristics of the self-crosslinkable PVDF-acrylic hybrid latex are: solids content = 45% by weight, latex particle size is 160 nm (zeta-average, measured by dynamic light scattering technique), PVDF-acrylic = 70/30 (mass ratio), acrylic polymer T_g is calculated as 23 °C based on the Flory-Fox equation, and DAAM is 8% by weight based on the acrylic portion. One comparable PVDF-acrylic hybrid latex with no keto-functionality was also made by replacing DAAM with other acrylic monomers while maintaining similar T_g of the acrylic portion.

One-component Waterborne Formulation

Table 1 outlines the one-component PVDF-acrylic-based waterborne formulation used in this study. The VOC of the prototype

formulation was calculated as 98 g/L, utilizing dipropylene glycol monomethyl ether (DPM) as a coalescing solvent. The pigment volume concentration was determined to be 13%. The paint was applied onto different substrates with a dry film thickness

of ~80 µm. The resulting coatings were allowed to dry at ambient temperature in the laboratory for 10 days prior to testing.

Dynamic Mechanical Analysis

The paints made with the self-crosslinkable PVDF-acrylic hybrid latex and its comparable PVDF-acrylic hybrid latex without keto-functionality were drawn down on a Teflon substrate with a dry film thickness of ~80 µm. After the films were dried at room temperature for 10 days, the films were peeled off the Teflon substrate and cut into strips for dynamic mechanical analysis (DMA).

DMA was performed at fixed frequency (1 Hz) and temperature from -100 °C to 150 °C on a Dynamic Mechanical Analyzer from Anton Paar. A sinusoidal stress was applied to the sample and the resultant displacement (strain) and phase lag (δ) were recorded as a function of increasing temperatures. The heating/ramp rate was 3 °C/min and strain amplitude within the linear viscoelastic region.

Detergent Resistance Test

The paints made with the self-crosslinkable PVDF-acrylic hybrid latex and its comparable PVDF-acrylic hybrid latex without keto-functionality were drawn down on polyvinyl chloride (PVC) and fiberglass-reinforced plastic substrate with a dry film thickness of ~80 µm. PVC substates were cleaned with isopropanol solvent wipe, and fiberglass-reinforced plastic substrates were flame-treated before being coated. After the films were dried at room temperature for 10 days, the coated substrates were subject to the detergent resistance test.

The detergent resistance test was performed according to AAMA 615/625 standard. A 3% (by weight) solution of detergent

with the formulation shown in **Table 2** as prescribed in ASTM D2248 was prepared in deionized water. At least two test coupons of the coated panels were immersed in the detergent solution at 38 °C (100F) for 72 h. Then the test coupons were taken out and dried using a towel. Immediately, the adhesion test was conducted per ASTM D3359.

The SSPC Paint 47 standard was developed for high performance fluoropolymer topcoats. In this standard, accelerated UV exposure is performed in a fluorescent UV/condensation apparatus complying with ASTM G154 with UVB 313 lamps, in accordance with ASTM D4587, using the following cycle: UVB 313 lamps, 8 h UV at 0.67 W/m2-nm at 60 ± 2.5 °C black panel temperature, 4 h condensation (no light) at 50 ± 2.5 °C. This 12-hour duration comprises one test cycle.

Weathering Test

Two gray paints were made based on the prototype formula in **Table 1.** One paint was made using self-crosslinkable PVDF-acrylic hybrid latex developed for this work. In comparison, the other paint was made using one commercial acrylic latex for durable exterior architectural coatings. The paints were drawn down on chromated aluminum Q-Panels (AL-412 from Q-Lab Corporation) with a dry film thickness of ~80 µm. After being dried at room temperature for 10 days, the coated panels were exposed to lab-accelerated UV per the SSPC Paint 47 Standard. The minimum total exposure time, 4000 h, was chosen for this study.

Dirt Pick-up Resistance Test

Two white paints similar to those used in the lab-accelerated UV exposure test were made by removing the Dynamix Black 30C965 from the pigment dispersion. The
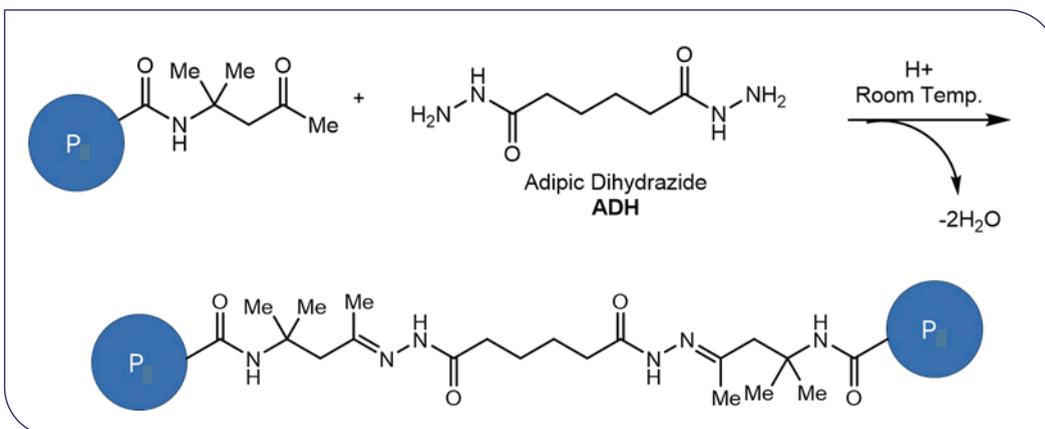
SCHEME 1
Keto-hydrazide self-crosslinking mechanism. P denotes the polymer chain.

Adipic Dihydrazide
ADH

paints were drawn down on chromated aluminum Q-Panels (AL-412 from Q-Lab Corporation) with a dry film thickness of ~80 μm. The dirt pick-up resistance (DPUR) test was carried out after the panels were dried at room temperature for 10 days.

DPUR was tested using an aqueous slurry comprised of 10% (by weight) hydrophobic carbon black (Birla Raven 22) and 0.1% (by weight) BYK 346 as a wetting agent. The slurry was applied onto the dried coating using a soft brush, allowed to sit at room temperature for 4 h, and then gently rinsed away with cold water and a paper towel. Then the color matrix (L*: lightness; a*: red/green coordinate; b*: yellow/blue coordinate) of the soiled versus unsoiled area of the coating was measured, and the color difference ΔE* was calculated based on **equation 1**:

$$\Delta E^* = \sqrt{((L_2^*-L_1^*)^2+(a_2^*+a_1^*)^2+(b_2^*-b_1^*)^2)}$$

Equation 1

A lower ΔE* indicates better DPUR.

Results and Discussion

Figure 4 shows the DMA of the dried films with and without keto-hydrazide crosslinking. The film with keto-hydrazide crosslinking exhibits a significantly higher storage modulus compared to the one without, suggesting crosslinking within the dried film.

The detergent resistance test is a crucial property assessment mandated by AAMA standards for aluminum, vinyl, and composite substrates. This test was conducted over PVC and fiberglass-reinforced plastic substrates. The formulated system with self-crosslinkable PVDF-acrylic hybrid latex successfully passed the detergent resistance test over both substrates, as shown in **Figures 5** and **6**, while the comparable system with PVDF-acrylic hybrid latex with no keto-functionality failed on both substrates.

Typically, keto-hydrazide crosslinking chemistry exhibits weak humidity performance in acrylic and polyurethane-based systems, largely owing to the reversible nature of the crosslinking bonds.[10] The robust detergent resistance test results in this study are likely attributed to the inherently hydrophobic properties of the PVDF chemistry. It is plausible that the PVDF polymer chains form a barrier, which inhibits water/humidity from hydrolyzing the keto-hydrazide crosslinking bonds.

FIGURE 4
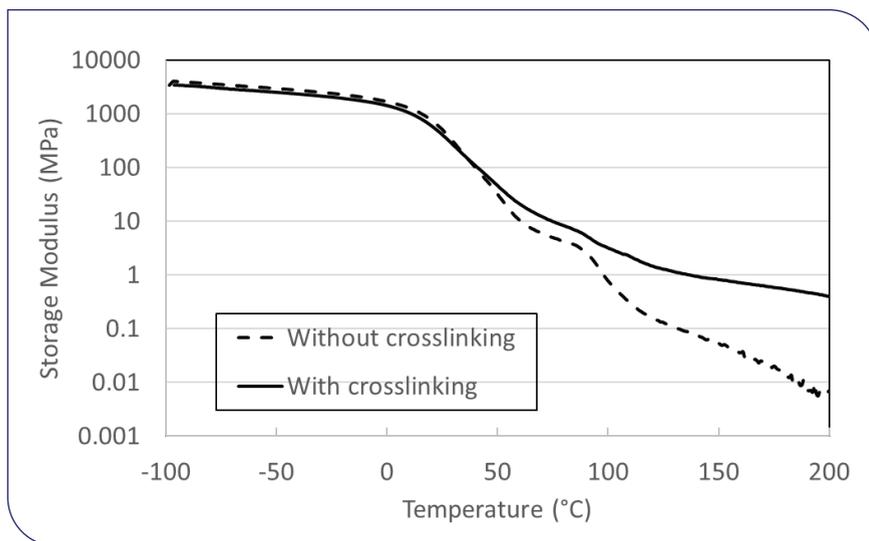**DMA of the dried films with and without keto-hydrazide crosslinking.**

FIGURE 5
Detergent resistance test of PVDF-acrylic coatings systems without (A) and with (B) keto-hydrazide crosslinking on PVC substrate.

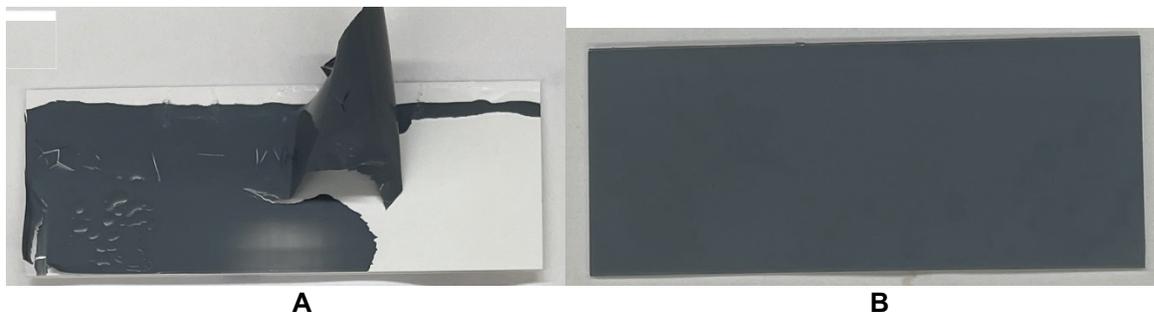

A   B

FIGURE 6
Detergent resistance test of PVDF-acrylic coatings systems without (A) and with (B) keto-hydrazide crosslinking on fiberglass-reinforced plastic substrate.
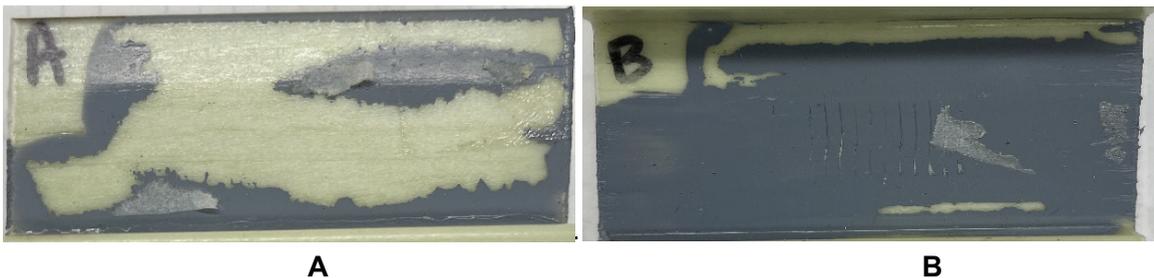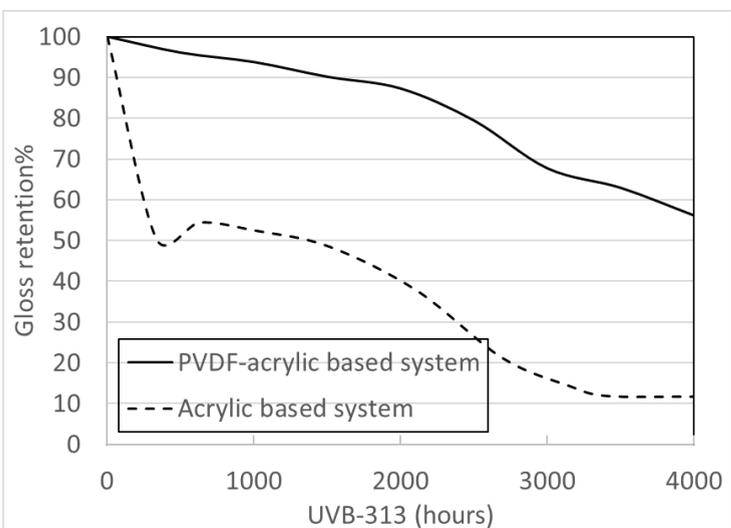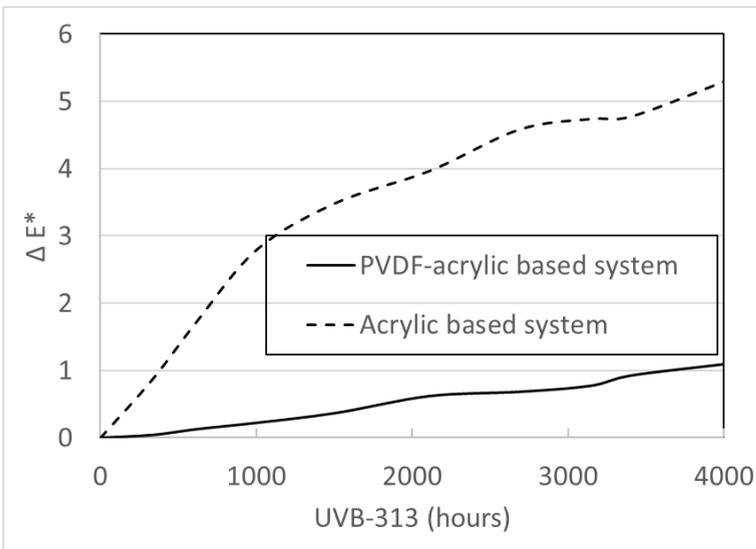

A   B

A

B

FIGURE 8
Dirt pick-up resistance (as measured by ΔE* color change after 4 h carbon black soiling at room temperature) for self-crosslinking PVDF-acrylic hybrid system (A, ΔE*=1.2) and acrylic-based system (B, ΔE*=27).

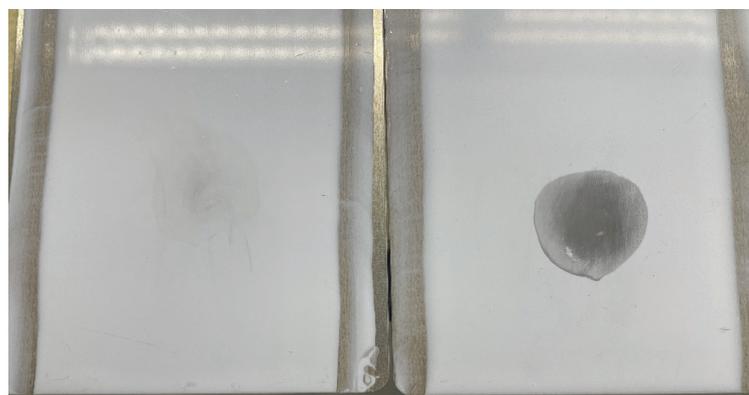**A**   **B**

Figure 7 shows that the self-crosslinking hybrid formulations can meet the accelerated weathering requirements in SSPC Paint 47 (gloss retention >50% and color retention (Delta E*) <5 after 4000 h UVB-313 lab accelerated weathering test).[9] For comparison, a commercially available weather-durable acrylic latex was chosen and formulated, as outlined in **Table 1**. As anticipated, the acrylic-based system showed significant deterioration in both gloss and color after 4000 h UVB-313 weathering.

The panels after dirt pick-up resistance testing are shown in **Figure 8**, demonstrating significantly superior performance of the PVDF-acrylic hybrid system compared to the acrylic-based architectural coatings system.

Conclusions

A novel self-crosslinkable PVDF-acrylic hybrid latex has been successfully developed which can be easily formulated into one-component self-crosslinking waterborne topcoats with VOC levels below 100 g/L. This versatile topcoat finds use in both OEM and field applications, offering exceptional durability for exterior coatings on architectural structures, water tanks, window and door frames, among others. Coatings formulated with this technology exhibit remarkable gloss and color retention during accelerated weathering testing. Moreover, the topcoat demonstrates strong adhesion to various substrates and successfully passes the detergent resistance test mandated by several AAMA standards. Notably, coatings based on this show superior dirt pick-up resistance and stay-clean properties, offering additional benefits over existing commercial acrylic and/or polyurethane-based topcoats. ✤

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