UV-curable fluoropolymer coatings for application at low temperatures

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Abstract

Fluoropolymer coatings for application at low temperatures, such as those based on Kynar® PVDF, have excellent weathering and flexibility but cure slow, lack hardness and chemical resistance. In contrast, UV systems cure fast, have great hardness and chemical resistance, but are rigid and don't weather as well as fluoropolymer coatings. At Arkema we are in the unique position of understanding both technologies and have developed UV-curable fluoropolymer systems that combine the best properties of each. These resins are weatherable, dirt and chemical resistant and have a good balance of flexibility and hardness. They can be used as clear or pigmented coatings for a variety of outdoor applications.

Introduction

Traditional homopolymer polyvinylidene fluoride (PVDF) coatings are commonly used in applications where resistance to UV degradation along with high mechanical properties are needed. The long fluoropolymer chains provide film integrity and flexibility while maintaining impact strength and resistance to a variety of chemicals. In order to create a homopolymer PVDF coating, the polymer is typically dispersed in a solvent and then baked at temperatures above 200 °C. Because of the high bake temperature, substrates are confined to those that are not heat sensitive such as metals[1]. Coatings based on PVDF copolymers have become popular due to their lower processing temperatures while still maintaining good weatherability. Compared to the homopolymer, however, the mechanical properties are not as robust, with some copolymer glass transition temperatures falling below zero, and the resulting coatings being relatively soft and having poor chemical and dirt resistance[2].

This leaves a gap for applications desiring weatherability coupled with hardness and scratch resistance in a coating, while maintaining relatively low processing costs. By creating UV-curable PVDF systems, one is able to impart high hardness and modulus to a traditionally softer material. This also decreases the required processing temperature as a lower temperature bake can be utilized without compromising the coating or the substrate. On the UV coating side, the PVDF increases the flexibility and weatherability, while allowing for a tack-free coating prior to curing. Figure 1 depicts the property space that each individual system occupies, along with the potential space that a hybrid system can achieve.

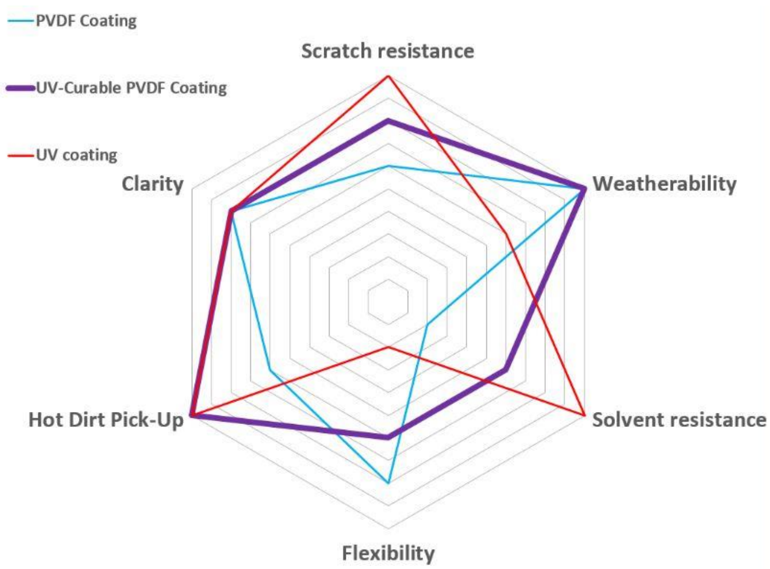

Figure 1. Coating System Comparison

Technical Approach

It quickly became apparent as we worked to develop a UV-curable fluoropolymer coating system that compatibility between the fluoropolymer and UV-curable (meth)acrylate portions is an important factor to consider. Many of our early attempts resulted in coatings that were very hazy and had uninteresting properties. In order to understand the composition space better a preliminary ladder study was done to evaluate the effect of the fluoropolymer/(meth)acrylate ratio (Table 1).

Table 1. Fluoropolymer/Acrylate Ratio Study

Fluoropolymer content	Acrylate content	Gloss on aluminum	Konig swings on aluminum
0.8	0.2	21.5	45.0
0.7	0.3	134.5	51.4
0.6	0.4	120.2	88.6
0.5	0.5	36.7	66.9

As can be seen in Table 1, the hardness and gloss of the coating varies greatly when adjusting the fluoropolymer/(meth)acrylate ratio. It is important to note that the coating with the highest hardness is not the one with the highest acrylate content. This demonstrates that there is a compositional sweet spot where optimum performance can be obtained. Although we expect the best composition ratio will vary based on the exact fluoropolymer and (meth)acrylate structures, for the sake of exploring the property space, all subsequent work reported in this paper was based on the composition ratio of 60/40 fluoropolymer to acrylate content.

Once the concentrations were established, the next parameter studied was (meth)acrylate composition. As with a traditional UV-curable coating, the functionality, backbone, and molecular weight all play an important role in dictating the final properties. In addition, compatibility between the fluoropolymer and acrylates must also be taken into consideration. Poor compatibility can result in precipitation of the polymer and/or poor coating quality. Phase separation may also occur after exposure to UV light and may produce a hazy coating.

Results and Discussion

A series of (meth)acrylate compositions with varying functionality and backbone structure were chosen in order to gain a better understanding of how these parameters affect the final properties. As mentioned previously, all the UV-curable fluoropolymer samples were made using the ratio observed to have the highest hardness. Each composition was then diluted with solvent to facilitate casting the coating on to the substrate, and an appropriate photoinitiator was added. Once the substrates were coated, the solvent was flashed off at room temperature for one hour and then at 60 °C for fifteen minutes. A high intensity mercury lamp was used to finish curing the samples, at which point they were left to condition in a controlled temperature and humidity environment for at least one day. The hardness, haze, and gloss of the cured samples are shown below, along with the breakdown of (meth)acrylate type in Figure 2 and Table 2 respectively.

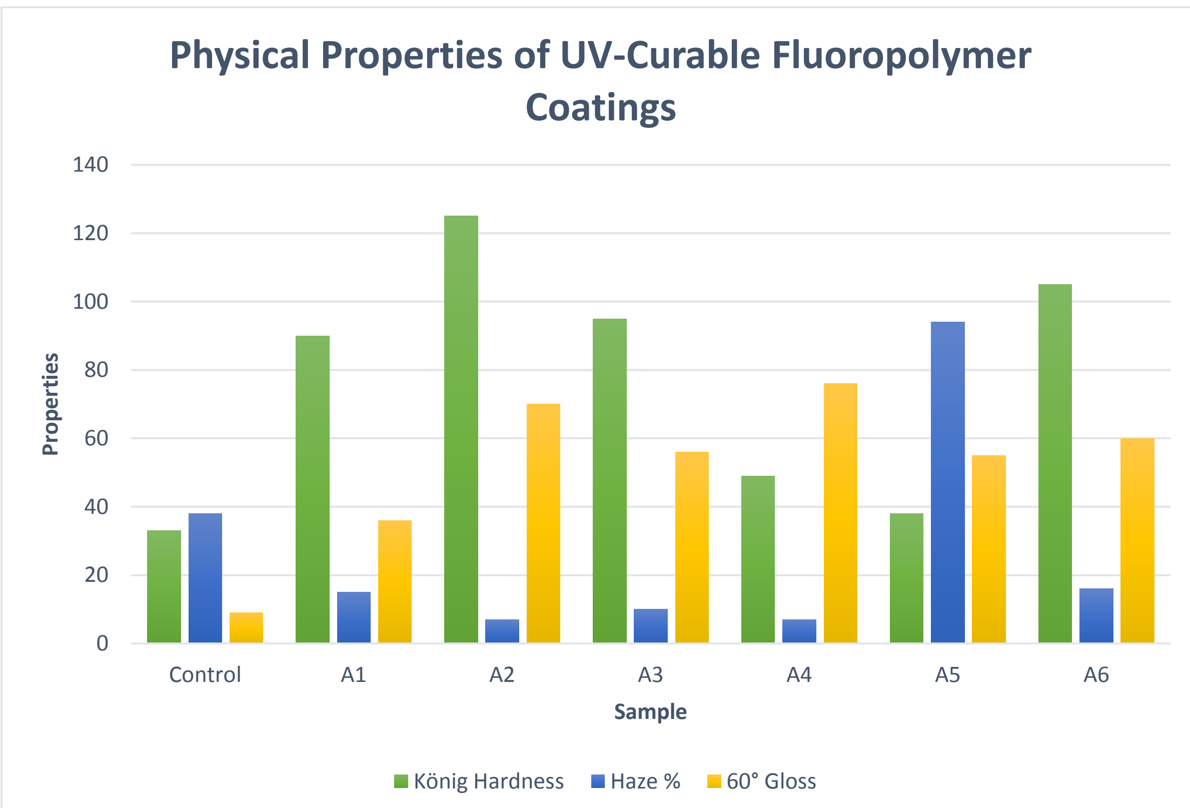

Figure 2. UV-Curable Fluoropolymer Coating Properties

Table 2. Acrylate Component Type

Sample Designation	(Meth)Acrylate
Control	None
A1	Difunctional Monomer
A2	Cyclic Difunctional Monomer
A3	Trifunctional Monomer
A4	Difunctional Urethane Oligomer
A5	Difunctional Polyester Oligomer
A6	Tetrafunctional Polyester Oligomer

With the UV-curable fluoropolymer systems we were able to achieve König hardness values over three times greater than the neat PVDF coating. This shows that the monomers and oligomers were mobile enough in the coating to crosslink and create an inter-penetrating network (IPN) around the PVDF chains. The A5 coating shows the lowest hardness value, which could be attributed to its high equivalent weight. A higher hardness was achieved using a tetrafunctional oligomer (A6) of the same backbone, showing that functionality plays an important role the larger the acrylate becomes. The highest hardness was seen in A2, which involved a cyclic difunctional monomer. The rigid structure of the monomer inherently provides high T_g properties to the coating, while the low molecular weight (relative to the polymer) allows it to create a tighter crosslinked network. A higher functionality (A3) did not seem to give a harder coating, implying once again that there has to be a balance between functionality and chain mobility during the UV-curing process.

Gloss measurements did not show any significant trends, with all the UV-cured samples showing a higher gloss than the control. The haze measurements were conducted on the samples after they were cured, or in the case of the control, baked. All but one of the samples showed a lower haze than the control; as the acrylates create a crosslinked network the crystalline PVDF structure is disrupted, resulting in a more amorphous/glassy morphology. The A5 sample is the only coating that had a higher haze than the control. This could be an indication of macro-scale phase separation between the fluoropolymer and the oligomer, resulting in a less robust IPN and therefore a lower hardness as seen in Figure 2. These results lead one to believe that as you increase the equivalent weight of the meth(acrylates), the more likely it will be for phase separation to occur, and the synergy between the two systems to be less pronounced.

Hot Dirt Pick-Up

As mentioned previously, fluoro-copolymer coatings tend to have good weatherability but are relatively soft. This can be an issue in exterior applications where the coating is exposed to not just UV, but also debris carried by wind or water. If the coating is too soft, it will pick up the debris and in some cases the coating can become permanently stained over time. Since UV-curable fluoropolymer coatings are harder than their traditional counterpart, it was of interest to see if the resistance to “dirt pickup” was improved as well. In order to gauge this property, we conducted a Hot Dirt Pick-Up test, or HDPU. Iron (II) oxide (FeO) and carbon black slurries were applied to the UV-curable fluoropolymer coatings, baked at 70 °C for two hours, and then washed off with water. A colorimeter was used to compare the "dirty" sections of the coating with a corresponding clean section. Results indicated the carbon black slurry consistently stained the coatings more than the FeO slurry. The Delta E (total color difference) of each stain test was averaged and compared between the different UV-curable fluoropolymer coatings as shown in Figure 3. A higher Delta E value is indicative of a coating with poor dirt pick-up resistance.

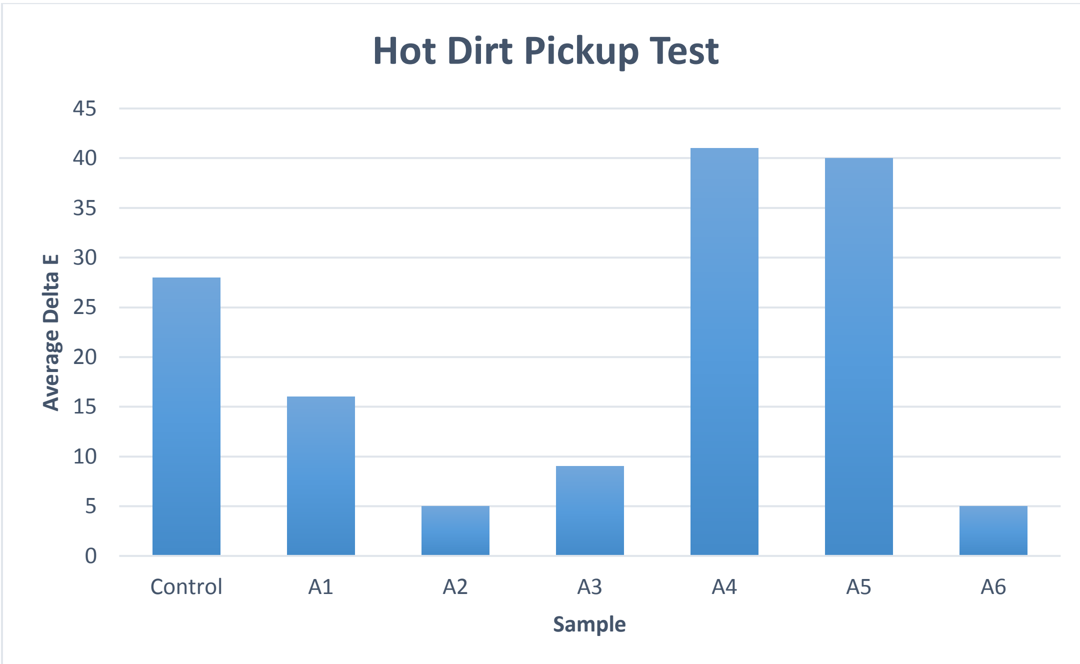

Figure 3. HDPU Results

As can be seen from the graph, the only coatings with higher Delta E values than the control are A4 and A5. These two coatings also showed the lowest König hardness values aside from the control (Figure 2). When the coatings with the lowest Delta E values (A2 and A6) are evaluated against their physical properties, one can see that they correspond to the coatings with the highest hardness values. These results indicate a positive correlation between hardness of the coating and its HDPU performance.

Weatherability

PVDF is known for its weatherability and has been shown to withstand over 15 years of UV exposure in exterior testing[1]. UV coatings have also been developed with similar properties, some showing little to no reduction in gloss or yellowing over 10 years[3]. In continuing to explore these combined systems, the goal will be to optimize mechanical performance while maintaining weathering resistance. Preliminary QUV B studies have shown minimal (< 20 %) change in gloss over 5000 hours[3]. Weathering tests on these hybrid systems are currently being conducted, from which a more comprehensive evaluation of data will be obtained.

Conclusion

UV-curable PVDF systems can be used to bridge the gap between traditional PVDF and UV-curable acrylic coatings. PVDF lends weatherability and flexibility to UV coatings in systems which would be brittle on their own. On the other hand, incorporating acrylic-functional components improves the mechanical performance of the softer PVDF. The end result is a weatherable, scratch resistant coating with more cost effective processing conditions and film integrity prior to free-radical polymerization. By changing the functional components of the system, one can tailor properties such as hardness, haze, gloss and stain resistance to fit the needs of their application.

References

(1) Iezzi, R.A., Gaboury, S., Wood, K., *Acrylic-fluoropolymer mixtures and their use in coatings*, 2000, pp. 55-60
(2) Arkema Internal Data
(3) Sartomer Internal Data