The Effect of Openair® Atmospheric Plasma on the Adhesion of UV Curable Coatings to Plastics

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Abstract

Ultraviolet (UV) cured liquid and powder coatings provide plastic part manufacturers with a number of desirable benefits including enhanced appearance, improved performance and various process advantages. At the same time, the rapid film formation and densely cross-linked chemistry that characterize UV curable materials also increases the likelihood of adhesion failures. That these coatings are formulated with little or no solvents makes attaining adhesion even more challenging. This paper examines adhesion problems inherent in UV curable liquid and powder coatings, and explores the tradeoffs associated with popular methods to mitigate adhesion problems. We find that atmospheric plasma treatment provides an especially effective means of improving adhesion of UV cure coatings to a wide range of plastic substrates.

Introduction to UV Coating Adhesion Failures

Since their emergence in the mid-1970s, UV curable coatings have continued to gain acceptance as a finishing method for a variety of substrates including many popular plastics. For example, nearly all automotive headlight lens assemblies, most eyewear, and a large portion of portable consumer electronics are UV coated. Several factors contribute to the popularity of UV cure materials compared to their thermal cured counterparts (Cohen, 2012).

First, UV cure processes are extremely rapid compared to conventional thermal curing and baking. Walton (2012) shows that while many conventional waterborne and solvent borne systems require substantial dwell time, UV formulations cure nearly instantaneously upon exposure to light. This makes UV curing particularly suitable for printing, optical fiber, graphic arts, wood coating, and other high-speed finishing applications. This process speed advantage is even more substantial when comparing traditional thermoset and UV cure powder coatings.

Conventional thermally cured powder coatings require a substantial amount of time to first melt and flow the powder, and then to achieve full cure through cross-linking. Walton (2012) reports that this two-stage process can commonly take from between 20 and 60 minutes depending on the powder chemistry and cure oven technology. By contrast, while UV curable powders rely on heat in order to melt and flow the powder to form a smooth film, they utilize UV energy for curing. Total processing times of less than 10 minutes have been reported in the literature (Schwarb and Knoblauch, 2011) .

Along with speed, UV formulations are noted for their surface properties, particularly scratch and mar resistance. These properties are responsible in part for the popularity of UV cure coatings for surfaces such as hardwood flooring, eyeglass lenses, and DVD coatings. These surface properties derive from the high cross-link density common in UV formulations such as those employing (meth-) acrylate chemistries (Schwalm, 2006). Film formation in UV materials is typically both rapid and densely cross-linked. This impacts the hardness of the film. Meichsner et al. (1998) find that E-modulus grows exponentially with cross-link density Xc according to:

$$\mathbf{E' = b'e^{mXc}}$$

A property closely associated with high crosslink density in UV coating films is physical shrinkage that occurs across the coating's surface during curing. The (meth-) acrylate monomers and oligomers common with free radical UV curing shrink considerably due to the replacement of longer-distance Van der Waals forces by strong but shorter covalent bonds. Jian et al. (2013) find that volume shrinkage causes build-up of internal stress, which results in defect formation, and dimensional changes responsible for decreased mechanical properties including adhesion. Schwalm (2006) reports that in UV formulations shrinkage can be as high as 35% of volume.

An attractive aspect of UV cure liquid coatings is the routine use of reactive diluents such as monomers and low molecular weight additives in lieu of conventional organic solvents. Since these constituents are consumed during the curing process, UV cure coatings are frequently promoted as high solids, even 100% solids formulations. This feature of UV cure coatings has received attention from both environmentally conscious manufacturers, and government regulatory agencies (Loof, 2001). While environmentally conscious manufacturers turn to UV cure because of the reduced hazardous air pollutants and VOCs, the absence of solvents contributes to the potential adhesion problem, since one function of solvents is to wet out the surface of the part.

Like UV coatings, powder coatings have been a finishing technology of interest to regulators such as the Environmental Protection Agency and industry leaders because of the generally referred to the “five E’s” of powder coating which include their business, organizational and environmental benefits.

- **E** fficiency
- **E** conomy
- **E** nergy Savings
- **E** nvironmental Compliance
- **E** xcellence of Finish

Powder coatings contain no solvents, and emit very little to no VOCs and hazardous air pollutants (Whitfield, 1995). But this lack of solvent to wet the surface makes adhesion more challenging, and most powder applicators must attend to proper pretreatment prior to powder coating.

Thus, many of those aspects of UV coatings that offer attractive benefits to their users also present formidable impediments to proper adhesion. Rapid film formation, along with high cross-link density results in mechanical stresses that combined with the lack of solvents reduces the likelihood of successful adhesion. It is not uncommon during the development of UV cure coatings to find that the cured film has the desired properties, but will not adhere to the part. Table 1 illustrates the surface energy of common plastics, and the needed energy required for adequate adhesion to a variety of coatings. On average, UV curable coatings require substantially higher surface energy to achieve adequate performance than their conventional counterparts.

Table 1. Plastic Surface Energy vs. Energy Required for Adhesion

Surface Energy of Common Plastics:		Approximate Surface Energy Needed for adhesion with:	
PTFE	< 20 mN/m		
PP	30	Waterborne Coatings	50-56
PE	32	Solvent Coatings	46-52
PS	34	UV Coatings	54-60
PC	34		
ABS	34		
PUR	34		

This paper proceeds as follows: first we review the most common approaches to improving adhesion of UV coatings to plastic substrates. Next, we highlight recent results that demonstrate the efficacy of atmospheric plasma to improve adhesion of UV liquid coatings. We conclude by presenting new data on the effects of plasma surface treatment on the adhesion of UV cure powder coatings to plastics.

Remedies for Improving Adhesion

Faced with inadequate adhesion, several remedies are available. These include reformulating the UV curable coating, modifying the composition of the substrate, adding adhesion promoting agents to the coating or applying an additional layer of coating, or by increasing free energy level of the substrate’s surface by means such as flame or plasma treatment (Ryntz, 1994).

Soils or contaminants on the plastic surface can limit adhesion. The first step is customarily to find a suitable cleaning agent, such as a solvent, to remove them. A concern with manual wiping of parts is worker safety due to exposure to harmful or caustic cleaners and solvents, and the hazardous VOCs emitted by these agents. Manual processing is time consuming, and for high speed processing, it may be more economical and efficient to use automated removal methods such as plasma ablation if the contaminant residue is thin.

Coating reformulation is another alternative, although it is sometimes difficult to reformulate without trading off other coating properties (Burak, 2003). Improvements in adhesion may come at the expense of loss of surface durability, change of gloss level, and a substantial increase in the cost of the coating. The willingness of chemistry suppliers to modify these properties can depend on the end-users willingness to pay for additional formulation and to suffer delays common with new iterations of coating development and testing. Where a coating has passed tests on standard substrates, reformulation may require requalification of the material, incurring additional testing time.

Reformulation of the substrate is another option. However, plastics are often selected for a range of manufacturing and mechanical properties such mold time, or dimensional stability. The material is often specified by the part designer and provides little latitude in finding a substitute that solves the problem since there are often few substitutes that provide these desired properties, or target cost per pound (Ryntz, 1998).

Since the weight of the part is generally much higher than the weight of the coating, modifying the plastic resin is generally more costly than modifying the coating since additives usually are dispersed throughout the entire cross section of the part, whereas only the surface requires modification.

Other methods have been developed which use a chlorinated polyolefin ‘tie-coat’ to assist in the adhesion of topcoats to untreated polyolefin. A thin layer (a few microns thick) of a dilute solution (35 wt %) of a chlorinated polyolefin (CPO) is applied to the substrate using a high solvent concentration. Proper adhesion depends critically on the thickness of the CPO layer. Too thick a layer will produce cohesive failure within the ‘tie-coat’ and with too a layer, adhesion to the substrate will not be attained (Ryntz, 1994).

An especially effective approach to improving adhesion is to modify the surface chemistry of the plastic. The saturated hydrocarbons that comprise much of the polymer surface are relatively inert when it comes to its affinity to bond with active species in the coating material. Improving adhesion between these two surfaces is a common application of plasma treatment.

Adhesion requires strong interfacial forces via chemical compatibility and/or bonding. Plasma can be used to modify surface energies. Hydrophilic and hydrophobic surfaces can be created on polymers through interaction with plasma. Using oxygen to create functionality increases the wettability of a surface. Figure 1 illustrates the effect of plasma on increasing the surface energy (mN/m) of a typical Polypropylene plastic.

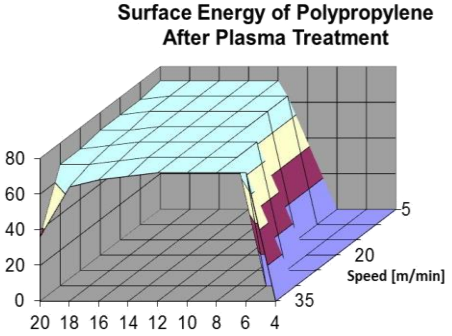

Figure 1. Surface energy following plasma surface treatment

The free electrons, ions, and radicals generated in atmospheric plasma impacts the surface with sufficient energy to cleave the molecular bonds on the surface of most plastic substrates. This cleavage produces free radicals on the polymer’s surface which react rapidly in the presence of air to form various chemical functional groups.

Highly polar functional groups that can form and enhance bonding include carbonyl (C=O), carboxyl (-COOH), hydroperoxide (-OOH), and hydroxyl (HO-) groups. Testing reveals that even relatively small amounts of reactive functional groups can be highly beneficial to improving surface characteristics and wettability.

Atmospheric Plasma Treatment of Plastics for Liquid UV Coatings

The beneficial effects of atmospheric plasma treatment have been established in the literature. Melamies (2012) demonstrates the efficacy of atmospheric plasma on polyamide fascia used for automotive interiors. Oehr (2003) reports the beneficial effects of plasma treatment or the coating of biomedical devices. Kaute (2003) reports that open air plasma can eliminate both the use of power washing and adhesion promoters for UV curing applications on plastics.

In recent work by Gururaj et al.,(2011) the effect of Openair® atmospheric plasma surface treatment on PC and PMMA plastics substrate panels (100mm × 100mm × 3mm) was evaluated. Panels were cleaned with isopropanol (IPA) prior to surface activation using atmospheric plasma.

Plasma was created with a compressed air at a supply pressure of 3 atm. and 100 liter/hour flow rate. The plasma power was maintained at 5 kW. A stationary Plasmatreat Openair® atmospheric plasma head with two nozzles separated apart by 80mm was employed in the test setup. The rotating plasma head rotates, generating an 80mm diameter with a substrate to plasma nozzle working distance of 10mm.

The panels were coated with a UV Silane-based material, cured using a three-medium-pressure-mercury lamp (120W/cm with 12kW wattage/lamp) on a conveyorized UV curing unit.

The effect of atmospheric plasma surface treatment on the wettability of the polymer surface prior to coating deposition was followed up by measuring the water contact angle. The water contact angle on the PC substrate was 80° ±2° before treatment and 43° ±1° after plasma treatment. The PMMA contact angle was 65° ±2° before and 55° ±2° after plasma treatment.

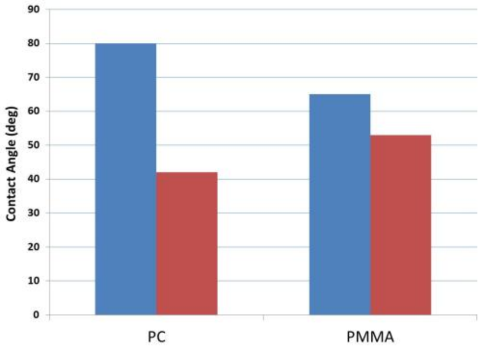

Figure 2. Change in Contact Angle with Plasma treatment.

Gururuaj et al. (2011) find that atmospheric Openair® plasma treatment successfully removes organic contaminants on the surface of the plastic and causes simultaneous surface oxidation. The free radicals produced, couple with active species from the plasma environment to form polar groups such as –(C–O)–, –(C O)– and–(C)–O– on the substrate surface. The significant decrease in contact angle measurements is a reflection of increase of surface free energy and greater adhesive strength between the polymer and UV coating.

UV Powder Coatings

UV powder coatings, commercialized during the late 1990's extended applications for powder coating beyond metal goods into markets using heat sensitive substrates such as plastics and wood.

UV Powders combine the cost efficiency, durability and environmental compliance of powder coatings with the faster speed and lower temperatures afforded by UV crosslinking (Mills, 1998). While acknowledging the potential benefits of UV cured powder coatings for a range of applications, the difficulty of achieving adhesion of the materials has also been recognized (Skinner, 2003).

Applicators report the use of a liquid primer prior to the application of UV powder to provide adequate adhesion (see Little, 2005). Knoblauch and Schwarb (2012) report good adhesion on a small range of plastic substrates using with a liquid primer coating.

Plasma Treatment for UV Powder Coatings

Method

This study examines the effect of plasma surface treatment on the performance of a UV cured powder coating on a wide range of popular plastic substrates. The method uses an initial atmospheric plasma pretreatment and activation step. Atmospheric plasma treatment is a safe and environmentally friendly alternative to traditional cleaning methods. The active species in the air combined with UV energy creates a chemical reaction with the surface contaminants, eliminating the need to manually clean the plastic. This process both cleans the surface by removing fine contaminants and increases the surface energy of the substrate.

Standard test plaques made of various blends of polypropylene, ABS, polycarbonate, ABS/Polycarbonate, and Nylon were used. Plasma surface treatment was done identically on each test panel at 20 FPM using a single nozzle Plasmatreat Openair® RD1004 rotating nozzle laboratory system, powered by an FG5001 power supply.

Following the Openair® atmospheric plasma surface treatment, a thin (10-12 micron) conductive coating (such as Chemical Technology Inc. CTI-4386 or CTI-1693 or similar product) is spray applied to promote electrostatic attraction of the powder coating. An acrylated polyester UV curable powder coating was electrostatically applied with a nominal film thickness of 50-60 microns.

The test panels were placed in a 110^{o}C convection oven for a total dwell time of 10 minutes. This was sufficient to allow the powder coating to melt and flow out over the surface of the substrate. The panels were then UV cured using a Gallium additive Mercury lamp (Fusion, 300W/in). Cure was confirmed using 50 double rubs of methyl ethyl ketone with no measurable loss of gloss on a 60^{o} gloss meter.

Results

At ambient temperature, each adhesion on each panel was evaluated using standard test method ASTM D 3359. The results of this testing is shown in Table 2 below:

Table 2. Adhesion results of UV powder coated substrates.

Substrate	Without Plasma	With Plasma
Polypropylene	0B	3B
ABS	0B	4B
Polycarbonate	0B	4B
ABS/Polycarbonate	4B	4B
Nylon 6	0B	0B

The data in Table 2 illustrates several interesting results. First, for a number of popular substrates the plasma treatment had a marked effect on adhesion properties. Polypropylene, ABS and polycarbonate had no adhesion without surface treatment, and very good adhesion following Openair® atmospheric plasma treatment. Second there is variation within these results that warrants additional process development. For example the polypropylene tested according to this method did not produce the same level of adhesion as we obtained on ABS or ABS/polycarbonate blends. (See Figure 3)

Further improvements in adhesion can be achieved with refinement of the surface treatment process and modifications to the powder melt/flow process. This highlights the need to optimize the process through laboratory testing prior to deploying a "stock" solution to the production floor.

We also note that some coating and substrate combinations (e.g. the ABS/polycarbonate blend used here) sufficiently work well without surface treatment, that the process provides little added benefit. Finally some substrates (e.g. the Nylon 6 tested here) did not show sufficient adhesion even with plasma surface treatment.

Discussion

It is important to note that this test regimen intentionally used a standard UV powder formulation and the same surface pretreatment method to test the robustness of the UV powder coating process on plastics.

With this proviso, we consider the results instructive. Four of the five substrates were successfully powder coated with good adhesion. In three of the four cases Openair® atmospheric plasma surface treatment made the difference between an acceptable and unacceptable process.

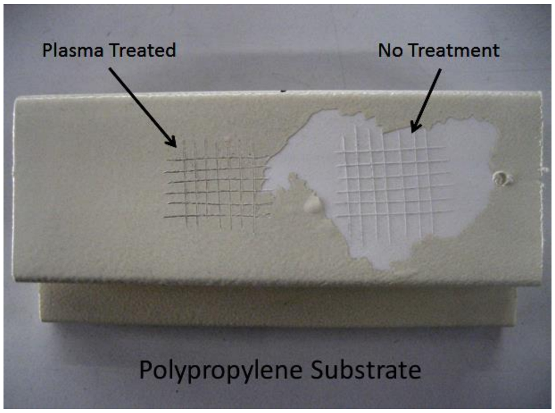

Figure 3. Effects of Plasma Surface Treatment on Polypropylene

As an avenue of future work, researchers are now testing variants of the powder coating, the melt/flow process and surface treatment parameters to optimize the adhesion on these substrates and to find a combination that will provide adhesion to Nylon, as well as extend the range of substrates to additional composites (e.g. BMC, PET, Nylon 66, SMC and others).

Conclusion

UV coatings are an attractive technology because of their excellent surface properties, low-heat and high-speed processing, and environmental compliance. The advent of UV curable powder coatings offers these benefits to powder coating, a technology recognized for its durability, and economic benefits owing to the efficiency of being able to reclaim over-sprayed powder coatings.

UV powders open the door to powder coating a range of heat sensitive substrates such a wood and plastic. However, many of the properties that provide these benefits to UV coatings also make adhesion to low surface energy plastic surfaces more difficult, and delamination of the fully cured paint film is a common occurrence with insufficiently prepared plastic substrates.

While various means exist to improve adhesion such as reformulation of the coating or plastic, these are time consuming and costly approaches. Other techniques such as manual cleaning are impracticable for high speed automated processes and require workers to handle frequently harmful solvents and dangerous VOCs which present both health and environmental and safety concerns.

This paper explores the role of surface treatment using atmospheric plasma treatment for overcoming difficult adhesion encountered with UV liquid and powder coatings. We find that there is strong empirical evidence that atmospheric plasma is effective at enabling UV liquid coating adhesion. A new series of testing also provides compelling evidence that atmospheric plasma surface treatment may provide a robust solution to applying UV powder to plastics.

While some work remains to be done in this area, our initial results demonstrate that atmospheric plasma treatment of substrates yielded acceptable or promising results on otherwise un-coatable surfaces in all but one substrate tested using a standard powder coating developed for general plastics application.

The use of safe, cost-efficient, and environmentally friendly atmospheric plasma appears to be an efficient means for improving the performance of both liquid and powder UV coatings for a growing range of plastic applications.

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