

Hooked on plastics: how to get your UV coating to stick to plastic?

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Abstract:

Plastic substrates especially thermoplastic polyolefins (TPOs) find increasing use in both Automotive as well as Industrial applications due to their superior flexibility, durability and lower cost. However, adhesion of UV coatings to these low surface energy substrates present challenges due to wide variation in surface properties for a given plastic substrate. We will present the results based on our adhesion study and starting point coating formulations for various plastic substrates using 3S (surface energy, swelling and shrinkage) approach.

Introduction

The use of various types of plastics as structural and decorative material has been growing for many years into a variety of applications. This includes end-uses in the container and packaging industry, in the automotive industry in both the interior and exterior of cars, and also in consumer and industrial applications. The articles being produced require printing or/and coating, but the sensitivity of plastics to heat (e.g. all thermoplastics, by definition) or to solvent attack put constraints on the type of coating or ink that can be used. Because radiation curing coatings or inks are natural contenders for use on such substrates, they are growing in use and popularity. Nevertheless, the adhesion of radiation curing coatings to certain plastics remains a challenge not only because of their low surface energy, but also due to wide variation in the surface properties for a given category of plastic. And the low surface energy plastic substrates, e.g. thermoplastic olefins (TPO's), are showing a very high growth in a variety of applications, as a result of their superior flexibility, durability and lower cost.

After reviewing the main parameters or factors that can influence or affect adhesion of radiation curing coatings to plastic substrates, this paper will present our proposal regarding possible solutions to get adhesion to difficult plastic substrates. To support this proposal, the performance of recently developed adhesion promoters is presented, as well as the methodology we are recommending for making the optimum selection of the components of the radiation curing formulation.

General considerations

Within the UV/EB curing coating market, only approximately 10% are coatings onto plastic substrates, pretty much dominated by coatings for PVC flooring. Although still limited, it is growing fast especially in certain sectors, mainly into automotive and consumer electronic applications. According to marketing consultants, the UV/EB plastic coating market shows higher growth rate and value than the overall UV/EB coating market.

The current biggest challenges for the formulators could be summarized as follows:

- The use of polyolefin-based materials, at the expense of plastics such as ABS, nylon and polyester is increasing, and they are much more difficult to adhere to than the plastics they are replacing.
- The adhesion problem is even more severe than with conventional solvent borne systems because swelling at the surface of the polymers does not occur with the vast majority of the radiation curing materials. In addition the latter are generally at the origin of significant film shrinkage, which results in weakening further the adhesion.
- Plastic substrates are increasingly being modified to bring new features to the surface that the coating needs to fulfill: it concerns the aesthetic (e.g. glamour color), the tactile feature (e.g. soft touch), the clean-ability (e.g. stain resistance) and the durability (e.g. scratch/mar resistance, non-yellowing).

- For the same type of polymeric substrate, differences are observed in surface conditions from supplier to supplier, from region to region, ...

The reasons for the poor adhesion of UV/EB curing coatings onto plastics can come from both the properties of the radiation curing system, as well as from the characteristics of the substrate.

1) Main properties of the radiation cured coatings affecting adhesion:

a) Shrinkage:

It is well known that upon exposure to radiation the transformation of the coating from liquid to solid results in volume shrinkage. The latter is mostly coming from the reactive diluents used in the formulation because they have high double bond per mole ratio and are present at high concentration, as they are responsible for reducing the viscosity of the (usually) high molecular weight oligomers. Table 1 presents the typical film shrinkage of various low-viscous acrylates, i.e. the change in the density of the formulation based on the acrylate and a photoinitiator (4% Darocur 1173, Ciba Specialties) during curing under UV-light (120W/cm).

Table 1:

Low-viscous acrylate (chemical name)	Abbreviation	Shrinkage (%)
Trimethylolpropane-triacrylate ^(a)	TMPTA	23.6
Trimethylolpropane-ethoxy-triacrylate ^(b)	TMP(EO)TA	16.9
Glycerol-propoxy-triacrylate ^(c)	GPTA	15.4
Hexanediol-diacrylate ^(d)	HDDA	13.1
Dipropylenglycol-diacrylate ^(e)	DPGDA	13.0
Bisphenol-A-ethoxy-diacrylate ^(f)	BPO(EO)DA	12.6
Tripropylenglycol-diacrylate ^(g)	TPGDA	12.3
Isodecyl-acrylate ^(h)	IDA	10.0
Neopentylglycol-propoxy-diacrylate ⁽ⁱ⁾	NPG(PO)DA	8.7
Neopentylglycol-propoxy-methyl-methacrylate ^(j)	NPG(PO)MEMA	6.0

(a): Photomer 4006; (b): Photomer 4149; (c): Photomer 4094; (d): Photomer 4017; (e): Photomer 4226; (f): Photomer 4028; (g): Photomer 4061; (h): Photomer 4810; (i): Photomer 4127; (j): Photomer 8127 are all commercial products from Cognis.

b) Stress

As it is a very fast process the radiation-induced polymerization of acrylates leads to the development of an internal stress into the coating. Since it is a much faster curing mechanism, this stress is developed at a much higher extent than in conventional thermal-curing coating.

c) Uncompleted reaction

The presence of unreacted materials at the interface between the coating and the substrate is generally a cause for adhesion failure. This is obviously more an issue with UV-curing systems than with EB-curing systems. Therefore, the type of UV-lamp, the type and level of photoinitiators, as well as the choice of oligomers and monomers is very important.

2) Main characteristics of the plastic substrates affecting adhesion:

a) Substrate wetting:

The surface tension for both the substrate and the wet (un-cured) coating should be considered with regards to substrate wetting. Table 2 presents the typical value (or range) for the surface tension of common plastic substrates.

Table 2:

Plastic Substrates	Surface Energy (mN/m)
Polypropylene (PP)	28 – 37
Polyethylene (PE)	31 – 36
Polyvinylchloride (PVC)	30 – 33
Polystyrene (PS)	34 – 45
Polycarbonate (PC)	~ 38
Thermoplastic olefins (TPO)	27 - 35

The surface tension of several low-viscous acrylate diluents, which is an inherent characteristic of the material, is shown in Table 3.

As a general rule: to wet well a substrate, coatings must have a lower surface energy than the substrate.

If every individual component of a formulation has its own surface tension, which cannot be changed, the surface tension of a coating formulation can be decreased by means of surfactants. But the selection of the surfactants can be very limited depending on the end-use, especially if the coating is used as a primer or an intermediate coating layer.

Table 3:

Monomers (abbrev.)	Surface Tension (mN/m)
NPG(PO)MEMA ^(a)	26
IDA ^(b)	29
NPG(PO)DA ^(c)	31
TPGDA ^(d)	34
DPGDA ^(e)	35
HDDA ^(f)	36

(a): Photomer 8127; (b): Photomer 4810; (c): Photomer 4127; (d): Photomer 4061; (e): Photomer 4226; (f): Photomer 4017 are all commercial products from Cognis.

On the other hand, the surface energy of a substrate, especially plastic substrates, can be increased by means of both chemical and physical treatments. The chemical treatments include mainly the following 2 treatments:

- i) Cleaning of the surface by using solvents or/and alkaline solutions as degreasing products.
- ii) Applying a chemical or coating primer to the surface. Its role is not to modify or affect the chemistry of the surface, but to provide adhesion for the subsequent coating layers.

Various types of physical treatment can be used to increase the surface energy of plastics, mostly through oxidation of the superficial layer. These physical treatments include:

- i) Flame treatment: quite widely used, e.g. for the treatment of cosmetic polyolefin tubes prior to printing, it consists of exposing the surface to be coated to a suitable oxidizing flame during a short period of time (0.2 to 3 sec.). The resulting change at the polymer surface improves dramatically its wet-ability and permits a strong adhesive bonding between the surface and the coating.
- ii) Corona treatment: very convenient as an in-line treatment of plastic films before printing, e.g. rotogravure printing of flexible packaging substrates, it consists basically in a strong oxidation of the surface by the ozone generated from the interaction of the electrical discharge and the oxygen (air). Depending on the type of polymer, the resulting increase in surface energy may disappear rapidly, i.e. within a few days.
- iii) Plasma treatment: obtained from the electrical ionization of a gas, the plasma (glow) discharge creates a homogeneous cloud of ionized gas, which raises the surface energy of the plastic substrate. Unlike this is the case for the Corona treatment, the plasma is created at much lower levels of voltage and temperature.

b) Substrate swelling:

Similarly to what is observed with solvents, although often to a lower degree, some monomers and oligomers can attack or swell certain plastic substrates, e.g. PVC, PC and PS in particular. This generally results in an improved adhesion of the coating to the substrate because an interpenetrating link may be established between the substrate and the coating. Due to their lower molecular weight, monofunctional and difunctional acrylate diluents tend to swell more plastic substrates than oligomers or higher-functional acrylate diluents. In our investigation, we have observed that the acrylate monomers and oligomers that are listed in Table 4 have the ability to swell plastics.

Table 4:

Monomers (abbrev.)	Oligomers (ref.)
HDDA ^(a)	PUA-1 ^(f) (<i>aliphatic PU-diacrylate</i>)
DPGDA ^(b)	PUA-2 ^(g) (<i>aliphatic PU-diacrylate</i>)
NPG(PO)MEMA ^(c)	
TPGDA ^(d)	
Lauryl-acrylate ^(e)	

(a): Photomer 4017; (b): Photomer 4226; (c): Photomer 8127; (d): Photomer 4061; (e): Photomer 4812; (f): Photomer 6010; (g): Photomer 6210 are all commercial products from Cognis.

c) Surface topography:

The surface topography of a substrate can also have an influence on the adhesion of a coating. Compared to a smooth surface, a rough surface offers a higher area of contact, thus a greater and more effective bonding area, and offers sites for mechanical interlocking for the polymer chains of the coating. Certain treatments, e.g. sanding or acid treatment, can be used to create or increase surface roughness.

The “Hooked on Plastics” Solution. Results & Discussion

1) The “hooked on plastics” solution = the “3S approach”:

Taking into consideration all the characteristics and parameters described above for both the substrates and the radiation-curable coatings, the present study was designed to probe the following concept:

In order to obtain a good adhesion to plastic substrates, the selection of the coating ingredients is critical and depends mainly on the 3 following properties of the monomers and oligomers:

- a) **Surface tension**
- b) **Shrinkage**
- c) **Swelling capability**

This is the reason for calling this product selection: ***the “3S approach”***.

Although the study has been focused primarily on the adhesion of the radiation-cured coatings to plastic substrates, attention should obviously also be given in the reality to other properties that are important for the application of the coating and the end-use requirements. This may include application viscosity, scratch and abrasion resistance, chemical resistance, flexibility, non-yellowing, ...

2) Experimental:

The materials used in this study are either fully commercial or only developmental at this stage, but they are all registered and can be sampled. In addition to the selection made within the commercial products on the basis of the so-called “3S approach”, some products were developed as adhesion promoters specifically for this study.

The selected products have been evaluated in the 2 simple formulations presented in Table 5:

Table 5:

Monomers (abbrev.)	Formula 1	Formula 1
Selected monomer/oligomer	20.0	73.0
"Label-free" diluted polyurethane-diacrylate ^(a)	73.0	20.0
HCPK ^(b)	2.0	2.0
HMPP ^(c)	5.0	5.0

(a): ECX-6025 (Cognis): diluted PU-diacrylate exhibiting good adhesion to various plastics;

(b): 1-hydroxy-cyclohexyl-phenyl ketone (Irgacure 184, Ciba S.C.);

(c): 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocure 1173, Ciba S.C.).

Coatings were applied (draw-down technique) at a thickness of approx. 6 µm, using a wire-wound rod, onto various plastic substrates (see Table 6) obtained from various sources.

Table 6:

	PC	PP	PE	PET	TPO	DF-1	DF-2
Surface Energy (mN/m)	38	38	38	39	< 31	> 42	39
Pre-treatment	none	Corona	Corona	Corona	none	none	none
Aspect	rigid	film	film	film	rigid	paper foil	plastic foil

PC = polycarbonate; PP = polypropylene; PE = polyethylene; PET = polyester; TPO = thermoplastic olefin; DF-1 = "decorative foil 1" (printed paper furniture); DF-2 = "decorative foil 2" (printed plastic furniture foil)

In order to limit as much as possible the influence of the curing state, all coatings were cured extensively by means of a very high UV-dose achieved by passing the coated substrate 2 times at a belt speed of 5 m/min. under 1 mercury lamp operating at 120 W/cm (UV-curing equipment from F.D.S.).

3) Successful products as adhesion promoter to plastics:

The adhesion to the substrates presented in Table 6 was assessed by means of the conventional cross-hatch adhesion tape test ("Crystal Scotch" cellotape, 3M). The products that have been found to provide excellent adhesion of at least one of the coating formula given in Table 5 are shown in Table 7, with their relative performance on all the substrates. In this Table, an "x" means that the product has provided 100% adhesion.

Table 7:

	PC	PP	PE	PET	TPO	DF
Adh. Prom. 1 ^(a)	x	x	x	x	x	x
Adh. Prom. 2 ^(b)	x	x	x	x	x	x
Acid-functional Olig-1 ^(c)				x		x
Acid-functional Olig-2 ^(d)					x	
Acid-functional Olig-3 ^(e)		x				
"label-free" diluted-PU-diacrylate ^(f)	x					

(a) = ECX-4114 (acrylated adhesion oligomer); (b) = ECX-5031 (modified ester/ether oligomer);

(c) = Photomer 4703; (d) = Photomer 4846; (e) = ECX-4046; (f) = ECX-6025; all products are from Cognis.

Note: the curing under UV-light of the coating formula containing the oligomer referred to as "Adh. Prom. 1", was observed to proceed more effectively when using benzophenone-type photoinitiators, e.g. Photomer 81, instead of the 2 photoinitiators mentioned in Table 5. Although

this product does not react fast, it cures much faster with benzophenone-type photoinitiator because it is acting also as a good hydrogen donor.

4) Formula suggestion for practical cases:

On the basis of the results that are summarized in Table 7 and in application of the so-called “3S approach”, we have developed coating formulations exhibiting excellent adhesion (100% adhesion at the x-hatch tape test) to substrates used in some specific end-uses. These formulations are described in the following paragraphs.

a) Coating for PVC flooring:

The substrate used in this application is plasticized PVC, which is characterized by the following features mainly: it is highly flexible and can undergo swelling rather easily.

The details of the coating formula that was developed and was meeting the requirements are given in Table 8. In addition, this coating has been designed to exhibit a high flexibility, as assessed by the bend test carried out on the coated substrate.

Table 8:

Ingredients	%	Explanatory comments
Aliphatic PU-diacrylate ^(a)	59.0	PU-based oligomer for adhesion
Ethoxylated Phenol-diacrylate ^(b)	8.0	
ESO-acrylate ^(c)	17.0	
Lauryl-acrylate ^(d)	8.0	Swelling monomer
Ethyl-hexyl-acrylate	4.0	Swelling monomer
HMPP ^(e)	4.0	

(a): ECX-6025 (Cognis); diluted aliphatic PU-diacrylate (Cognis); (b): Photomer 4039 (Cognis);

(c): Photomer 3005 (Cognis); (d): Photomer 4812 (Cognis);

(e): 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocure 1173, Ciba S.C.).

b) Coating for polycarbonate display rack:

The substrate used in this application is a hard and thick extruded polycarbonate; the main feature to take into consideration is that it can swell or be attacked very easily. The details of the coating formula that was developed to meet these requirements are given in Table 9.

Table 9:

Ingredients	%	Explanatory comments
Aliphatic PU-hexaacrylate ^(a)	40.0	High scratch resistance PU-acrylate
HDDA ^(b)	15.0	Swelling monomer
ESO-acrylate ^(c)	5.0	
Adh. Prom. 1 ^(d)	15.0	Adhesion promoter
NPG(PO)DA ^(e)	20.0	Low surface tension & low shrinkage
BP / 4-methyl-BP liquid blend ^(f)	5.0	

(a): Photomer 6623 (Cognis); (b): Photomer 4017 (Cognis); (c): Photomer 3005 (Cognis);

(d): ECX-4114 (Cognis); (e): Photomer 4127 (Cognis); (f): Photomer 81 (Cognis).

c) Primer for TPO (car bumper):

The substrate used in this application is TPO, which is characterized by the following features mainly: low surface energy, non-porous, high chemical resistance. The details of the primer formula that was developed and was exhibiting excellent adhesion to this difficult plastic substrate are given in Table 10.

Table 10:

Ingredients	%	Explanatory comments
Adh. Prom. 1 ^(a)	15.0	Adhesion promoter
NPG(PO)DA ^(b)	20.0	Low surface tension & low shrinkage
BP / 4-methyl-BP liquid blend ^(c)	5.0	

(a): ECX-4114 (Cognis); (b): Photomer 4127 (Cognis); (c): Photomer 81 (Cognis).

d) Laminating adhesive for PP/paper laminate:

The plastic substrate used in this application is a polypropylene (PP) film, which is characterized by the following features mainly: low surface energy, non-porous and very flexible. As this is the case for making PP/paper laminate currently, the plastic film is Corona treated prior to the application. In Table 11 are reported the details of the laminating adhesive formula that was developed and provided excellent adhesion to PP, as assessed by the delaminating test, where the paper could not be detached from the PP film without tearing.

Table 11:

Ingredients	%	Explanatory comments
Adh. Prom. 2 ^(a)	78.0	Adhesion oligomer
TMPTA ^(b)	15.0	
HCPK ^(c)	2.0	
HMPP ^(d)	5.0	

(a): ECX-5031 (Cognis); (b): Photomer 4006 (Cognis); (c): Irgacure 184 (Ciba S.C.); (d): Darocure 1173 (Ciba S.C.)

In Summary

The solution that we have probed in the present study and are proposing to make the optimum selection of the monomers and oligomers to formulate coatings exhibiting good adhesion to plastic substrates is the so-called "3S approach". It consists in making the selection on the basis of the following characteristics:

1. SHRINKAGE: should be as low as possible; low functionality diluents are preferred.
2. Capacity to SWELL the substrate: certain monomers and oligomers have been identified.
3. SURFACE TENSION: as low as possible to help wetting of the plastic substrate.

The following factors are also worth considering when formulating radiation-curing coatings for plastic substrates:

- Each grade of plastics needs to be evaluated separately, since there are so many parameters that can vary in the production or/and processing of plastics.
- Whenever feasible, adjustment of the surface energy of plastics by means of pre-treatment will not only facilitate adhesion, but also ensure reproducibility.