

UV CURABLE COATINGS – OPTIONS FOR CHALLENGINNG SUBSTRATES

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The use of UV curable coatings continues to expand into applications that have traditionally been the domain of other coating technologies. UV curable materials offer the advantages of faster cure times, shorter production lines, greater energy savings and a reduced environmental impact. UV curable materials are now found in a number of different applications. These include wood coatings, vinyl flooring, metal coatings, flexible packaging films, electronic assemblies, as well as numerous other applications. However, some of the applications involve challenging substrates and require more specialized formulations utilizing special functionalities capable of achieving optimal substrate adhesion and the desired final performance. The inclusion of UV compatible adhesion promoters for challenging substrates that may be helpful in obtaining optimum adhesion. In addition, some of the advantages accompanying the advent of UV LED curing technology will be discussed.

SUBSTRATES UTILIZED

One of the most important flexible substrates used in the industry is biaxially oriented polypropylene (BOPP). It is mechanically rugged and has a high chemical resistance.¹ It is used in a variety of roles including packaging and adhesive tape applications. However, due to their low hydrophilicity, low surface energy and lack of functional groups on its surface, these films pose a challenge for inks and adhesives for durable coatings.

Polyethylene Terephthalate Glycol (PETG) is a transparent, high gloss film used in medical, food packaging, thermoforming and electronic applications. It is a modified (by co-polymerization) version of PET which was patented in 1941 and later given the trademark Mylar by E.I. DuPont.² By design and application, it is heat sensitive.

Cast polypropylene film usually known as CPP film is widely used in packaging. It is one of the most common films used for metalization.³ CPP Films are widely used in Food and confectionary, Oil and Lube, Detergent & Shampoo, Textile, Pouch & Bag, Pharmaceutical Tablet, disposable syringe, needles and medical appliances blister packing.

Shown below are the FTIR spectra of both surfaces of the five substrates. They reveal that one side of each substrates, except for PETG, has been treated to improve adhesion.



Fig. 1: FT-IR of BOPP substrate

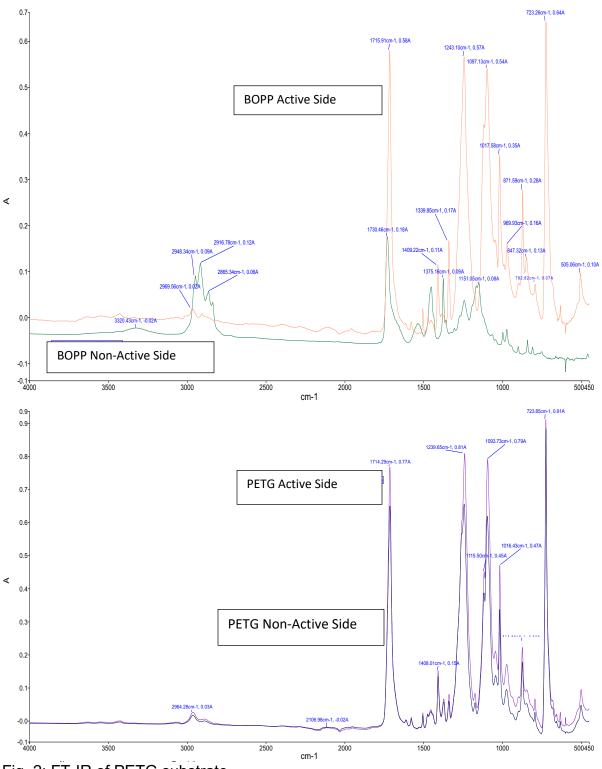


Fig. 2: FT-IR of PETG substrate



Fig. 3: FT-IR of CPP substrate

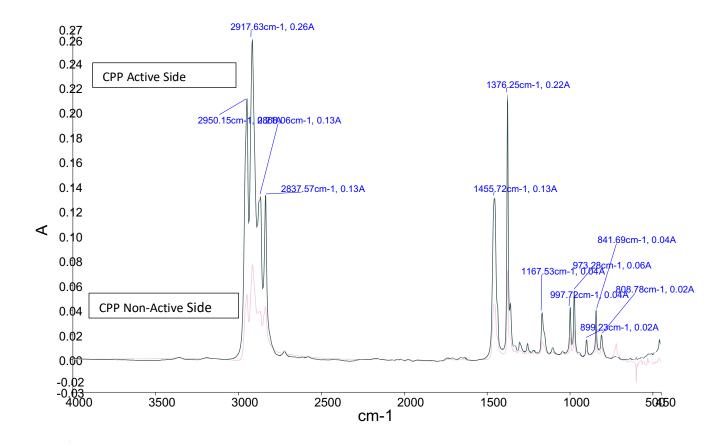
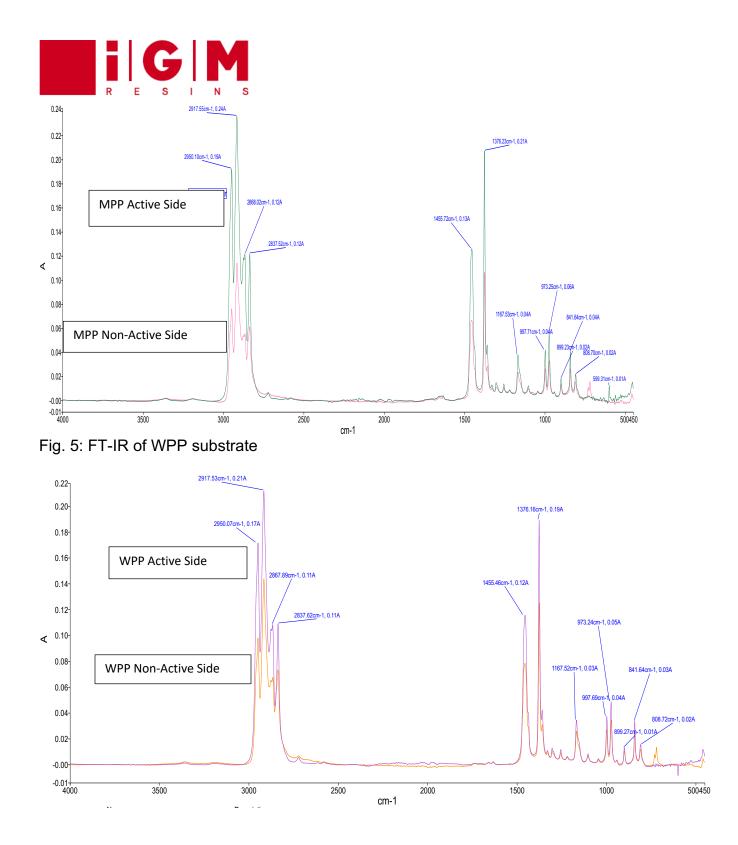


Fig. 4: FT-IR of MPP substrate



Surface energy is a key parameter in determining the wettability of a substrate. Lower surface energy materials will wet higher surface energy substrates. The first table below provides the reported surface energies of some common polymer substrates. The second table shows the surface energies of the substrates above, as they were measured for this evaluation.



<u>Table 1: Surface Energy of Common Polymers¹ (Dyne/cm)</u>

Polytetrafluoroethylene (PTFE)	18.5
Silicone	24
Poly (vinylidene fluoride)	25
Polyethylene (PE)	31
Polypropylene (PP)	31
Polystyrene	33
Poly (vinyl chloride) (PVC)	39
Nylon-6,6	43
Poly (ethylene terephthalate) (PET; Polyester)	43

Table 2: Surface Energy of Substrates Evaluated

Film	Surface Energy*
	(outer surfaces)
Clear PP	40 Dyne/cm
White PP	40
Metalized PP	38-40
BOPP	44+
PETG	30

*Approx. by Dyne pens

UV CURABLE MATERIALS TESTED

The adhesion of five different Photomer acrylate materials from IGM to the polymer films above were evaluated in this study. One of their key attributes is adhesion improvement.

TABLE 3: Adhesive Materials information

Photomer Product	CAS#	Description	Functionality	Viscosity @ 25C, cPs	Attributes
4173 [®]	30697-	Acid	1	4000	Adhesion, Hardness
	40-6	Functional			
4703 [®]	50940-	Acid	1	190	Adhesion, Chemical
	49-3	Functional			Resistance
4046 [®]	57043-	Acid	1	5750	Adhesion, Hydrophobicity
	35-3	Functional			
4846 [®]	13048-	HDDA,	2	750	Adhesion, Flexibility
	33-4	diluted with			-
		polyester			
		resin			
4039 [®]	56641-	Modified	1	30	Adhesion, Flexibility
	05-5	Phenol			-
		Acrylate			



TABLE 4: Adhesive Formulation information

Formulations	CL-1-1023-	CL-1-1012-	CL-1-1023-	CL-1-1023-	CL-1-1023-
Used	32A	32B	32C	32D	32E
Photomer 4173 [®]	97.0%				
Photomer 4703 [®]		97.0%			
Photomer 4046 [®]			97.0%		
Photomer 4846 [®]				97.0%	
Photomer 4039 [®]					97.0%
MBF (photo-	3.0%	3.0%	3.0%	3.0%	3.0%
initiator)					

TABLE 5: Surface Energy Information of Cured Adhesive films

Cured Formulation	Surface Energy*
(Acrylate)	(outer surfaces), Dyne/cm
32A (4173®)	40
32B (4703®)	40
32C (4046 [®])	42
32D (4846 [®])	40
32E (4039 [®])	<_30

*Measured over WPP Films with Dyne Pens.

COATING PROCESS

As shown below, the films were attached to steel Q-panels and then coated with #4 Draw Down Rod (for a film thickness of approximately 1 mil/25 microns) using the draw down technique.

Figure 6: Substrate preparation for coating



Films mounted for coating and curing.

CURING PROCESS

A Fusion UV oven equipped with a Type H Mercury vapor bulb was used to cure the coatings. Samples were passed through the UV oven three times at a line speed of 63 fpm. The coatings were cured immediately after application.

Figure 7: UV curing station





TEST METHODS

- Tape adhesion⁴: The standard tape test using 3M Brand 600 tape in which a length of tape (2.0" minimum) was applied to the sample, pressed to remove entrapped air and then rapidly and forcefully removed (at a right angle to the test area. A new unused strip of tape was used for each test.
- 2) Tape adhesion on folded sample: The coated film sample was folded over 180 degrees. Any cracking or delamination at this point was noted. Then 3M Brand 600 tape was applied to the folded area and forcefully removed. Any lifted or peeled coating was noted.
- 3) Crosshatch tape test⁵ (not used on film samples): A standard multiblade cutter was used to make two perpendicular sets of cuts into the coating. Any flaking or peeling was noted. Then a strip of 3M Brand 600 tape was applied. The entrapped air was pressed out and then the tape was forcefully removed. Any lifting or peeling of the coating was noted.

RESULTS

In the tables below, a check mark " 🖋 " indicates that the sample passed the evaluation. An "X" indicates failure.

WPP	Photomer 4173 [®]	Photomer 4703 [®]	Photomer 4046 [®]	Photomer 4846 [®]	Photomer 4039 [®]
Surface Tack	Very Slight	Slight	Very Slight	None	Slight
Tape Adhesion	✓	✓	~	Х	<
No Crack on Fold	Х	~	<	Х	Х
Adhesion on Fold	Х	<	~	Х	<

Table 6: Evaluation Results for WPP substrate

Table 7: Evaluation Results for MPP substrate

MPP	Photomer	Photomer	Photomer	Photomer	Photomer
	4173 [®]	4703 [®]	4046 [®]	4846 [®]	4039 [®]
Surface Tack	Very Slight	Slight	Very Slight	None	Slight



Tape Adhesion	✓	<	~	Х	<
No Crack on Fold	~	V	✓	Х	<
Adhesion on Fold	<	~	~	Х	✓

Table 8: Evaluation Results for CPP substrate

CPP	Photomer 4173 [®]	Photomer 4703 [®]	Photomer 4046 [®]	Photomer 4846 [®]	Photomer 4039 [®]
Surface Tack	Very Slight	Slight	Very Slight	None	Slight
Tape Adhesion	✓	✓	~	<	<
No Crack on Fold	✓	<	<	Х	<
Adhesion on Fold	V	V	<	Х	<

Table 9: Evaluation Results for BOPP substrate

BOPP	Photomer 4173 [®]	Photomer 4703 [®]	Photomer 4046 [®]	Photomer 4846 [®]	Photomer 4039 [®]
Surface Tack	Very Slight	Slight	Very Slight	None	Slight
Tape Adhesion	~	>	~	\checkmark	<
No Crack on Fold	>	V	<	Х	<
Adhesion on Fold	<	<	<	<	<

Table 10: Evaluation Results for PETG substrate

PETG	Photomer 4173 [®]	Photomer 4703 [®]	Photomer 4046 [®]	Photomer 4846 [®]	Photomer 4039 [®]
Surface Tack	Very Slight	Slight	Very Slight	None	Slight
Tape Adhesion	~	✓	<	<	<
No Crack on Fold	~	<	<	<	<
Adhesion on Fold	<	<	 ✓ 	<	<

Figure 8: Visual of Tape on crease test





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Passed - PH4046<sup>®</sup> on MPP
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Failed - Tape on Crease - PH 4173®

In the next evaluation, the coatings were applied at a thickness of about 12 microns. Though there were some differences, particularly for the WPP and MPP films, the results were similar overall.

WPP	Photomer 4173 [®]	Photomer 4703 [®]	Photomer 4046 [®]	Photomer 4846 [®]	Photomer 4039 [®]
Tape Adhesion	~	~	~	>	~
No Crack on Fold	~	~	<	Х	~
Adhesion on Fold	✓	~	~	Х	~

Table 11: Evaluation Results for WPP substrate @ 12um FT

*No adhesion loss, but stress cracks seen.

Table 12: Evaluation Results for PETG substrate @ 12um FT

MPP	Photomer 4173 [®]	Photomer 4703 [®]	Photomer 4046 [®]	Photomer 4846 [®]	Photomer 4039 [®]
Tape Adhesion	Х	V	~	Х	~
No Crack on Fold	Х	V	<	Х	<
Adhesion of Fold	Х	<	★ *	Х	<

*No adhesion loss, but stress cracks seen.

Table 13: Evaluation Results for CPP substrate @ 12um FT

CPP	Photomer 4173 [®]	Photomer 4703 [®]	Photomer 4046 [®]	Photomer 4846 [®]	Photomer 4039 [®]
Tape Adhesion	<	<	<	<	<
No Crack on Fold	~	~	<	<	<
Adhesion of Fold	√	√	≮*	<	<

*No adhesion loss, but stress cracks seen.

Table 14: Evaluation Results for BOPP substrate @ 12um FT



BOPP	Photomer 4173 [®]	Photomer 4703 [®]	Photomer 4046 [®]	Photomer 4846 [®]	Photomer 4039 [®]
Tape Adhesion	<	<	<	♦	<
No Crack on Fold	V	V	<	\$	<
Adhesion on Fold	~	V	<	<	<

Table 15: Evaluation Results for PETG substrate @ 12um FT

PETG	Photomer 4173 [®]	Photomer 4703 [®]	Photomer 4046 [®]	Photomer 4846 [®]	Photomer 4039 [®]
Tape Adhesion	~	~	<	<	<
No Crack on Fold	~	~	<	<	<
Adhesion on Fold	Х	√	∢ *	<	~

*No adhesion loss, but stress cracks seen.

For comparison, several other materials Photomer 4226 (Dipropyleneglycol diacrylate), Photomer 4017 (Hexanediol diacrylate), Photomer 4034 (HECLA) and Photomer 4184 (2[[Butylamino) carbonyl]oxy] ethyl acrylate) were evaluated on the five films. As shown below, PH4034 and PH4184 performed very well. Though HDDA performed well in the Tape test on the films, overall, PH4226 and PH4017 did not perform as well as the five materials specifically recommended above as adhesion promoters.

Table 16: Evaluation Results for PH4226

PH4226 [®] (DPGDA)	BOPP	PETG	CPP	WPP	MPP
Tape Adhesion	Some	<	Х	Х	<
	Cracks				
No Crack on Fold	Х	Х	Х	Х	Х
Adhesion on Fold	Х	Х	Х	Х	Х

Table 17: Evaluation Results for PH4017®

PH4017 [®] (HDDA)	BOPP	PETG	CPP	WPP	MPP
Tape Adhesion	>	~	>	♦	<
No Crack on Fold	Х	Х	Х	Х	Х
Adhesion on Fold	<	<	Х	Х	Х

Table 18: Evaluation Results for PH4034®



PH4034 [®]	BOPP	PETG	CPP	WPP	MPP
Tape Adhesion	>	>	<	<	V
No Crack on Fold	>	>	V	<	V
Adhesion on Fold	>	>	V	V	V

Table 19: Evaluation Results for PH4184[®] Reference

PH4184 [®]	BOPP	PETG	CPP	WPP	MPP
Tape Adhesion	>	>	♦	\$	>
No Crack on Fold	<	<	<	<	<
Adhesion on Fold	>	>	V	V	V

Coatings on Glass

Glass can sometimes be a challenging substrate, particularly if it is treated with tin-oxide. Unfortunately, due to the non-availability of suitable samples of this material, a common craft type glass was used for this evaluation.

Tape Adhesion⁵ and Crosshatch Tape Adhesion⁶ tests were performed with the results shown below.

Glass (~42-44 Dyne)	Photomer 4173 [®]	Photomer 4703 [®]	Photomer 4046 [®]	Photomer 4846 [®]	Photomer 4039 [®]
Surface Tack	Very Slight	Slight	Very Slight	None	Slight
Tape Adhesion	✓	<	<	<	<
Crosshatch Tape Adhesion	~	~	<	Х	<

Figure 9: Crosshatch Tape Adhesion Test on Glass



Photomer 4046[®] on Glass



SUMMARY

As noted, all the adhesion promoting materials performed better, overall, than the control materials, DPGDA and HDDA, on the packaging films.

The results for each Photomer adhesion promoting acrylate are summarized below. These materials may be used as adhesion promoting additives in UV formulations for packaging materials or they may be used by themselves, where suitable, as a primer layer.

Tape Adhesion Test Performance

Product	CAS#	Description	@ 25um	@ 12um
Photomer 4173 [®]	30697-40-6	Acid Functional	Passed tape adhesion on all five substrates.	Passed tape adhesion on BOPP, PETG, CPP and WPP.
Photomer 4703 [®]	50940-49-3	Acid Functional	Passed tape adhesion on all five substrates	Passed tape adhesion on all five substrates
Photomer 4046 [®]	57043-35-3	Acid Functional	Passed tape adhesion on all five substrates	Passed tape adhesion on all five substrates
Photomer 4846 [®]	13048-33-4	HDDA diluted with Polyester resin	Passed tape adhesion on BOPP, PETG, CPP and MPP.	Passed tape adhesion on BOPP, PETG, CPP and WPP.
Photomer 4039 [®]	56641-05-5	Modified Phenol Acrylate	Passed tape adhesion on all five substrates.	Passed tape adhesion on all five substrates.

Tape Test on 180⁰ - Fold

Product	CAS#	Description	@ 25um	@ 12um
Photomer	30697-40-6	Acid Functional	Passed test	Passed test
4173 [®]			on BOPP,	on BOPP,
			PETG, CPP &	CPP and
			MPP.	WPP.



	3		
50940-49-3	Acid Functional	Passed test	Passed test
		on all five	on all five
		substrates	substrates
57043-35-3	Acid Functional	Passed test	Passed tape
		on all five	adhesion on
		substrates	all five
			substrates
13048-33-4	HDDA diluted	Passed test	Passed test
	with Polyester	on BOPP &	on BOPP,
	resin	PETG.	PETG, CPP
			and WPP.
56641-05-5	Phenol Acrylate	Passed test	Passed test
	-	on all five	on all five
		substrates.	substrates.
	13048-33-4	50940-49-3Acid Functional57043-35-3Acid Functional13048-33-4HDDA diluted with Polyester resin	50940-49-3Acid FunctionalPassed test on all five substrates57043-35-3Acid FunctionalPassed test on all five substrates13048-33-4HDDA diluted with Polyester resinPassed test on BOPP & PETG.56641-05-5Phenol AcrylatePassed test on all five

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