UV FLEXO INK COMPOSITION AND SURFACE TREATMENT EFFECTS ON ADHESION TO FLEXIBLE PACKAGING

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ABSTRACT

UV flexo inks are becoming increasingly popular in flexible packaging and shrink sleeve applications, traditional markets for flexographic inks. The ever-increasing improvements in UV flexo inks such as print quality, low ink maintenance requirements, no solvents, high press stability, and in-line finishing have all contributed to converters' decisions to switch to UV flexo system. Recently, new UV flexo ink systems have improved efficiency and production speeds to greater than 250 meters/minute. However, variables such as resin selection, amount of ink applied, substrate absorbency, UV curing conditions and print speed can all propagate episodes of erratic adhesion on difficult substrates. Hence, many substrates are coated with a primer to perform as adhesion promoter. Nevertheless, this additional coating are not always successful, increase cost to the convertor and typically do not mitigate the migrating effect of lubricating additives found within certain flexible packaging films. This paper will detail, in the absence of adhesion promoters, the effects of corona, flame or atmospheric plasma surface treatments on the adhesion of UV flexo inks to flexible packaging films.

INTRODUCTION

UV flexo technology is quickly establishing itself as a bridge to sustainability within the graphic arts markets. Historically, energy-curable systems were used in surface printing applications (PSA labels, shrink sleeves, in-mold, food packaging, etc.) where the properties of cured UV inks and coatings led to improvements in abrasion resistance compared to solvent- and water-based inks. It was also found that UV inks performed well with UV and EB coatings used in flexible packaging structures. Currently, UV flexo inks are being applied on the internal and external surfaces of a broad range of high performance packaging structures. In addition, UV flexo inks provide a significant step toward sustainability by eliminating/reducing the emissions of VOCs and CO2.

Generally speaking, the drying of a conventional ink film occurs when the ink solids (resins, additives, pigment, etc.) coalesce into a film on the substrate surface accompanied by evaporation of volatiles and/or penetration into the base substrate. In some cases, conventional inks require several hours for complete drying. With energy-cured materials, the majority of the components in the ink or coating remains on the surface of the substrate and are chemically converted within seconds to a hard surface "film" following exposure to UV or EB energy. The difference between these processes lies in the chemistry of the materials in the inks and coatings, and in the technology required to energize the curing process.

The formulation of UV flexo inks with low viscosity, high color strength, high cure speeds and adhesion is a considerable challenge for ink formulators. The rheology of UV flexo inks is significantly improved with measured combinations of resins, additives and pigment wetting vehicles. Oligomers are the primary resins in an energy-cured ink and provide basic ink properties, while monomers are used primarily for viscosity reduction. [1] Relative to optimizing anchorage of these oligomer-monomer carriers to the substrate, surface modification by corona, flame or atmospheric plasma all have potential to do so because of their efficient surface roughening and functionalizing effects.

This collaborative study was undertaken to understand the potential synergistic interactions between different atmospheric pressure surface modification techniques and different oligomer types in UV flexo ink formulations, and the overall impact of these synergies on ink adhesion to various unprimed, flexible polymer-based surfaces.

EXPERIMENTAL

Ink Materials:

All monomers and oligomers used for this study were supplied by Cytec Industries (Smyrna, GA).

Table 1. Oligomers evaluated

Products	Description	Functionality	Viscosity (cP @ 25C)
EBECRYL® 83	Amine Modified Polyester Acrylate	3.5	515
EBECRYL 3702	Fatty Acid Modified Epoxy Acrylate	2	495,000
EBECRYL 4883	Aliphatic Urethane Acrylate	2	161,000
EBECRYL 860	Epoxidized Oil Acrylate	4	26,500
EBECRYL 5801	Polyester Acrylate Bioligomer	3	6,000
EBECRYL 450	Fatty Acid Modified Polyester Acrylate	6	8,200
EBECRYL 3703	Amine Modified Epoxy Acrylate	2	320,000
EBECRYL 4827	Aromatic Urethane Acrylate	2	238,000
EBECRYL 3720	Bisphenol-A Epoxy Acrylate	2	750,000

The photoinitiator used for this study and also supplied by Cytec Industries (Smyrna, GA), Additol DX, is a proprietary, eutectic blend of photointiators designed to provide both surface and through cure.

Surface Treatments:

Surface modification (summarized in Table 2) of the films was completed by Enercon Industries Corp., Menomonee Falls, WI. The following types of treatment were performed:

1) Universal corona discharge - Technology is a dual dielectric corona system, employing a ceramic electrode assembly and ceramic-covered ground roll, high voltage/low frequency transformer and power supply.
2) Flame plasma discharge - Technology employs a high velocity, CNC fabricated port burner with removable port inserts, water cooled lateral ports integral to the burner assembly, chilled treater roll, electronic combustion/gas mixing controls, and integrated electronic oxygen analyzer.

3) Atmospheric plasma discharge – Technology employs proprietary plasma electrode and ground plane, power supply and transformer. Gas chemistries are regulated and electronically mixed prior to introduction to the treatment station.

Table 2. Surface Modification Trial Protocol

			Plasma				
Material	**Corona**	**Flame**	**Carrier %**	**Reactive %**	**Power Density (W/ft2/min.)**	**Initial mN/m**	**Final mN/m**
PLA	CU				1	35	42
PLA	CU				1	35	42
PLA		FM			1100 lpm/1200fpm	35	42
PLA		FM			1100 lpm/1200fpm	35	42
PLA			Nitrogen/95	CO2 / 5	1	35	42
PLA			Nitrogen/95	CO2 / 5	1	35	42
PET	CU				1	36	44
PET	CU				1	36	44
PET		FM			1100 lpm/1200fpm	36	44
PET		FM			1100 lpm/1200fpm	36	44
PET			Nitrogen/95	CO2 / 5	1	36	44
PET			Nitrogen/95	CO2 / 5	1	36	44
Met. OPP	CU				2.6	30	44
Met. OPP	CU				2.6	30	44
Met. OPP		FM			1300 lpm / 500fpm	30	44
Met. OPP		FM			1300 lpm / 500fpm	30	44
Met. OPP			Nitrogen/95	CO2 / 5	2.6	30	44
Met. OPP			Nitrogen/95	CO2 / 5	2.6	30	44

Universal corona discharge technology was chosen because of its homogeneous discharge relative to covered roll and bare roll discharges, offering a higher potential for surface adhesion. The flame plasma technology employed utilized CNC-drilled high velocity port burner assemblies and a double-coated chill roll with electronic mass flow control of air and natural gas inputs at a 10:1 ratio, respectively, and electronic oxygen content control. Atmospheric plasma treatment ionized a mixture of nitrogen and carbon dioxide using electronic mass flow controls at high frequency. The uncoated films used in the study are described in Table 3 below.

Table 3. Films evaluated

Material	**Supplier**
Biaxially oriented PLA 4042D, 20 microns	NatureWorks®

AET MT metalized, BOPP film, 18 microns	AET films
Uncoated PET	Teijin DuPont Films Japan Ltd.

Testing:

Bench-evaluations were completed at Cytec Industries using hand-held flexographic print instruments equipped with a 360 line screen anilox roll and a metal doctor blade. All bench-produced prints were cured in a Fusion Aetek UV unit set at 150 fpm and using 400W/inch mercury lamps in an air environment. Exposure was 120 mJ/cm2.

Starting formulations identified by bench-evaluation were subsequently tested on a two-unit Aquaflex LC-1002 printing press using the same films as in bench-testing. Press evaluation was completed at line speeds between 150 and 350 feet per minute (fpm). On press, the inks were printed with a 700 line screen/2.43 BCM anilox roll and cured with one of Fusion's Aetek UltraPak 400W/inch lamps.

Adhesion was tested after ink cure using 3M 610 Scotch Tape® on an unscored print surface. Prints from bench testing were rated for ink adhesion using a relative scale of 1 – 5, with 1 = poor and 5 = excellent. Prints from press trials were evaluated for adhesion by visually assessing the quantity of ink left on the substrate after tape removal. A percent value was assigned to the amount of ink remaining, with no ink removal = 100% adhesion and complete ink removal = 0% adhesion.

RESULTS

Defining the monomers (s) to be used for the study

During pre-study work with monomers, a fatty acid modified polyester acrylate was used as the base resin in a blend with the monomer being evaluated and photoinitiator. The monomer evaluation showed positive adhesion results (Table 4) with TMPTA, HDODA, IBOA and TRPGDA. IBOA was eliminated due to the high odor associated with this material and HDODA was eliminated due to its tendency to attack and swell photopolymer printing plates.

Table 4- Evaluation of reactive diluents and monomers

Monomer		Reactivity	Adhesion	Flexibility
Isobornyl Acrylate	IBOA	1	4	5
Octyl/Decyl Acrylate	ODA	1	3	5
Tripropylene Glycol Diacrylate	TRPGDA	3	3	4
1,6-Hexanediol Diacrylate	HDODA	3	5	3
Trimethylopropane Triacrylate	TMPTA	5	4	3
Propoxylated Glycerol Triacrylate	GPTA	5	2	2
Trimethylolpropane Ethoxy Triacrylate	TMPEOTA	4	2	2

Reactivity, adhesion and flexibility were assessed on a scale of 1-5, 1=poor and 5=excellent

From the results of table 4, the monomers chosen for further evaluation in the UV inks for press trial were Trimethylolpropane triacrylate (TMPTA) and Tripropylene glycol diacrylate

(TRPGDA) in a 1:1 ratio to combine the reactivity of TMPTA and the flexibility offered by TRPGDA.

Defining the oligomer (s) to be used for the study

As part of the study, oligomers and monomers were assessed for basic properties on metalized OPP, PET and PLA film substrates. Samples of each of the three substrates were treated with the three types of surface treatment previously mentioned. The selected oligomers were diluted with Trimethylopropane Triacrylate (TMPTA) to a viscosity of 500 mPa.s @ 25°C. After dilution, 10% Additol DX liquid photoinitiator blend was added to each sample. The oligomer/monomer/PI blends were then printed on the substrate samples and each print was assessed for tape adhesion and the results are listed in Table 5 below.

Table 5 – Bench evaluation to define oligomers for the press trials: adhesion results

	PET			Metalized OPP			PLA		
	Corona	Plasma	Flame	Corona	Plasma	Flame	Corona	Plasma	Flame
Amine modified polyester acrylate	1	1	2	2	1	2	3	2	3
Fatty Acid modified epoxy acrylate	2	2	3	1	1	2	2	2	2
Acrylate Aliphatic Urethane Acrylate	3	3	3	3	2	3	2	2	3
Epoxidized Oil Acrylate	2	3	4	2	2	3	4	4	5
Polyester Acrylate Bioligomer	4	3	5	3	3	4	4	2	4
Fatty Acid Modified Polyester Acrylate	5	4	5	4	3	4	4	3	4
Amine Modified Epoxy Acrylate	2	3	2	3	2	1	2	2	1
Aromatic Urethane Acrylate	1	2	1	2	3	3	2	1	1
Bisphenol-A Epoxy Acrylate	1	1	2	1	2	1	2	1	1
TOTAL	**21**	**22**	**27**	**21**	**19**	**23**	**25**	**19**	**27**

Adhesion was assessed on a scale of 1-5, 1=poor and 5=excellent

As shown in table 5, differences were identified in adhesion with generally increased adhesion to the corona- or flame-treated films compared to the plasma-treated films. Also, it was noted during the study that surface energy, and ultimately ink adhesion, of the flame-treated substrates deteriorated within 2-3 days. The plasma- and corona-treated films retained surface energy for a significantly longer period (up to 10 days) but while ink adhesion was maintained on the corona-treated film as surface energy deteriorated, ink adhesion was significantly reduced on the plasma-treated substrates.

The differences in adhesion were further analyzed by 1) overall adhesion by film and treatment types and 2) overall adhesion by oligomer type. The data used for this analysis are outlined in Tables 6 and 7 below.

Adhesion analysis by film and treatment types (table 6) indicates that certain surface treatments may be better suited for different film polymers. As a result, optimizing the surface treatment and film combination may be another option, if conditions allow, to obtain increased ink adhesion – in addition to ink modification.

Table 6 – Overall adhesion by film and treatment types

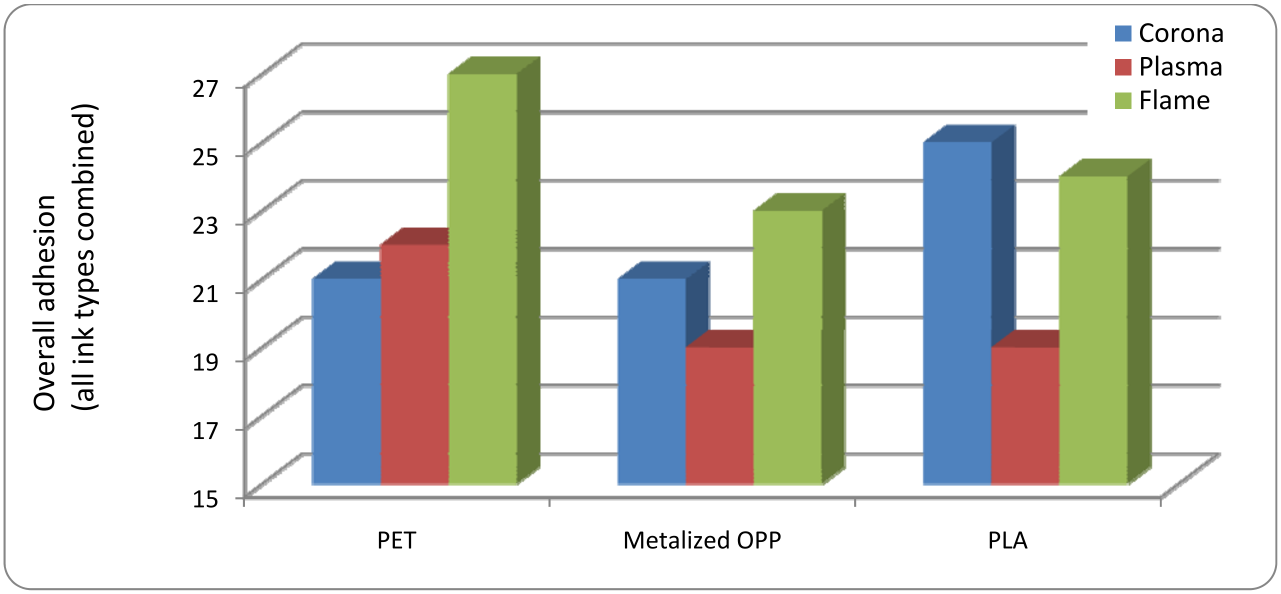
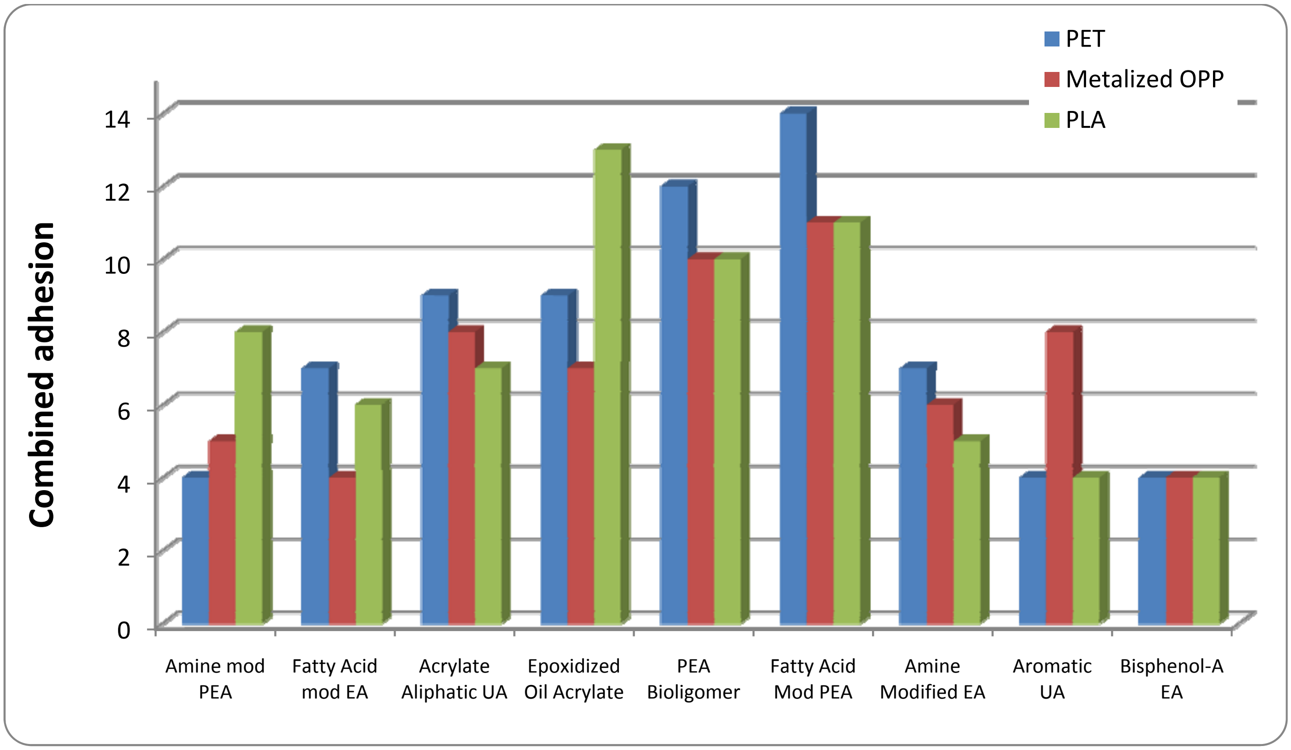


Table 7 – Overall adhesion by film and oligomer types



Analysis of adhesion based on film and oligomer types (table 7), indicates that the ink composition, specifically oligomer selection, significantly affects adhesion. This review was used, in part, to help select the final ink composition.

Based on the results discussed above, it was decided to perform further evaluation for this study using the top performing oligomer groups; fatty acid modified polyester acrylate and polyester acrylate bioligomer. The starting formulation selected for further study is defined in table 8 below.

Table 8- Ink starting point formulation

Pigment	18%
Oligomer	35%
Monomer(s)	37%
Photoinitiator	10%

RESULTS WITH FINAL FORMULATIONS

The final two ink formulations identified by bench-evaluation were subsequently tested at Cytec Industries on a two-unit Aquaflex LC-1002 printing press using corona-treated OPP and PLA films as in bench-testing. Additional PET film was unavailable at the time of testing. The other treatment types used with the OPP and PLA films were also evaluated at 150 fpm and at 350 fpm in the Fusion Aetek UV unit.

At relatively low line speeds (150 fpm), acceptable adhesion was obtained with both inks on both films and with all treatment types. As the line speed increased, adhesion to the corona-treated films was maintained with the ink based on the fatty acid modified polyester acrylate but was reduced with the polyester acrylate bioligomer.

The reduction in adhesion might be related to a difference in reactivity between the two oligomers. Also, at higher line speed adhesion to the plasma-treated films appeared to be less than adhesion to the other two types of surface treatments.

It must be noted that the final ink formulations tested did not contain modifying resins and/or additives that are commonly used in ink formulating to increase adhesion or tape release. The following is a summary of the adhesion results with the final ink compositions.

Adhesion results with final ink formulations

		OPP			PLA		
		Flame	Plasma	Corona	Flame	Plasma	Corona
Polyester Acrylate Bioligomer	150 fpm	80%	80%	95%	85%	75%	95%
	350 fpm	50%	50%	65%	25%	25%	50%
Fatty Acid Modified Polyester	150 fpm	90%	90%	95%	90%	90%	95%
	350 fpm	80%	75%	85%	90%	70%	90%

Adhesion was visually assessed.
The % reported is the approximate ink coverage remaining in the tape area after the tape is removed.

CONCLUSIONS

Specific formula modifications, with additives and modifying resins, will be necessary to provide optimum adhesion on a case-by-case basis. However, the following are the general trends, results and observations from this evaluation:

1. Oligomer and monomer selection must be completed to match the type of film and film surface treatment used to prepare the substrate for printing.
2. Differences in ink adhesion can be easily identified when the ink is printed on the same base film finished with different surface treatments. At higher line speed, adhesion to the plasma-treated film is less than adhesion to the corona- and flame-treated samples of the same film.
3. As the treated substrates age, ink adhesion to the flame-treated film deteriorates rapidly within a few days while adhesion to the plasma- and corona-treated films remain for a longer period.
4. Fatty Acid Modified Polyester Acrylate-based ink displayed better adhesion than the Polyester Acrylate Bioligomer-based ink especially at increased press speed. Therefore, if the “green” property is desired in both film (e.g. PLA) and ink, optimization must be completed with the ink composition to find the best balance of properties.
5. The levels and types of monomers commonly used to improve ink adhesion, e.g. HDODA, must be evaluated and optimized in order to obtain the best ink adhesion while avoiding damage to the flexographic printing plate.

REFERENCES

[1] Seecharan, A. et al, “Energy Cure (EC) Flexographic Inks for PLA Films”, RadTech UV&EB Conference Proceedings, 2008.