Energy Cure (EC) Flexographic Inks for PLA Film

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Abstract

Packaging film manufactured using polylactic acid (PLA) derived from corn has recently emerged as an alternative to petroleum-based films. Since corn is a renewable resource, the environmental advantage of PLA film is immediately obvious with the main marketing driver for PLA film being the use of a sustainable bio-based resource for manufacture. Other expected advantages include compostability or recyclability, a natural surface energy of approximately 38 dynes/cm which should facilitate ink adhesion, high clarity, and suitability for high shrink applications. PLA film is produced in various thicknesses in gloss, matte or opaque forms. The various types of film may be used for applications such as food trays, folding cartons, shrink sleeves, lids, envelope windows and packaging overwrap.

Notwithstanding the natural high surface energy of PLA film, ink adhesion may be less than ideal because of the apparent presence of a surface layer possibly from migratory additives. In the laboratory, removal of this surface layer by wiping results in improved ink adhesion. In commercial application, corona treatment within a short time of printing coupled with a sound stock rotation system may be necessary to ensure consistent adhesion. Alternatively, corona treatment in-line with printing may be used.

The use of energy curable (EC) flexo inks on PLA film is currently being explored with consistent adhesion being the main challenge to date. In addition to adhesion, ink flexibility and reactivity must be optimized for specific applications. This presentation will provide an introduction to the applications of PLA film as well as details on work to develop EC flexo inks for use on PLA film.

Introduction

Awareness of bio-based packaging materials, including PLA films, has increased significantly over the last five years partly driven by concerns about global warming and its possible connection with use of petroleum-based products. Use of bio-based films is increasing in food and beverage markets as these films are used for pouches, shrink and roll-fed labels, flexible packaging and food trays. The use of these bio-based products will likely accelerate in the short term because of:

1. regulation – especially in Europe
2. cost reduction as supply of PLA film increases coupled with rising oil prices
3. marketing by brand owners around carbon footprint reduction
4. consumer demand for environmentally-friendly products
5. mass marketers requiring a supply base which incorporates sustainable materials

Growth estimates for bio-based films are typically 20-30% year on year dependent on the rate at which the supply chain is developed. However, consumer adoption of the relatively new technology will depend a great deal on how well convenience, safety and cost compare to the established petroleum-based products.

Based on supplier data and marketing information, the main attributes of the bio-based films used in printing and packaging applications are:

1. a natural high surface energy, without treatment, which enhances print quality and adhesion
2. properties (clarity, flexibility, heat resistance, etc.) similar to petroleum-based products, after modification
3. biodegradable, compostable and recyclable options

On the other end of the spectrum, the main challenges to be considered as the technology and markets evolve will include:

1. a possible draw on food resources which causes food prices to increase
2. infrastructure for optimal disposal of bio-based films
3. suitability for microwaveable, hot-fill and extreme storage conditions
4. shelf-life of a packaging material which decomposes – especially in a heated environment
5. possible equipment and ink modification to accommodate the new substrates
6. differences in functional properties, e.g. gas barrier and migration resistance

At this time, a relatively small quantity of PLA film is being converted and, when printed, one of the three major ink systems (water-based, solvent-based and energy-cure) is involved. In some cases, ink adhesion is less than perfect off-press but because it improves over time after printing, the converter will accept this deficiency with a new technology in the short-term. As the use of PLA film increases, this lack of immediate adhesion will become a major liability in a market requiring short turnaround time. This challenge in addition to the basic properties of ink lay/leveling, flexibility and reactivity were examined in the energy-cure flexographic ink study associated with this paper.

Experimental Procedures

Commercial rolls of EarthFirst PLA Shrink Label Film and EarthFirst PLA Label Film were purchased from Plastic Suppliers Incorporated, and used for laboratory evaluations and flexographic press trials. (EarthFirst is a registered trademark of Plastic Suppliers Incorporated.)

Raw material screening involved testing acrylated oligomers for basic properties of reactivity, flexibility and adhesion. Based on the results from the oligomer evaluation, selected acrylated oligomers were then tested with monomers to identify possible advantages from monomer selection. The most encouraging oligomer/monomer combinations were then evaluated in starting point ink formulations for basic application properties.

Evaluations were initially completed using bench testing with typical laboratory equipment on label grade PLA and shrink grade PLA films. Reactivity, flexibility and adhesion were tested on both substrates and relative performance ratings were assigned. Starting formulations identified by bench evaluation were subsequently tested on a two-unit Aquaflex brand printing press using the same films used in bench testing.

Bench evaluations were completed using hand-held flexographic print equipment equipped with a 360 line screen anilox roll and a metal doctor blade. All bench-produced prints were cured in one of Fusion's Aetek UV units set at 150 fpm using one 300W/inch "H" Mercury lamp in an air environment. Exposure was 120 mJ/cm^2.

Press evaluation was completed with blue ink, printed at line speeds between 150 and 350 feet per minute (fpm). On press, the blue ink was printed with a 360 line/4.8 BCM anilox roll and cured with one of Fusion's Aetek UltraPak 400W/inch lamps.

Reactivity was tested by checking for print mar or damage using a wooden tongue depressor with a mar-free surface indicating good reactivity. Adhesion was tested after cure using 3M's 610 Scotch Tape on an unscored print surface. Relative performance ratings were assigned. It was observed that the tape test method affected the test results. Using a relatively constant speed of tape removal appeared to provide higher adhesion results vs. using an erratic pull of the tape. The constant speed method was selected for reporting since the results appeared more consistent between samples.

The flexibility/wrinkle test involved holding a print with thumbs and forefingers and with hands approximately 1 to 2 inches apart. The print was rotated in a clockwise direction for 20 cycles and then in a counter-clockwise direction for 20 cycles. The print was observed for ink removal and/or print damage, and a relative performance rating was assigned.

Results and Discussion

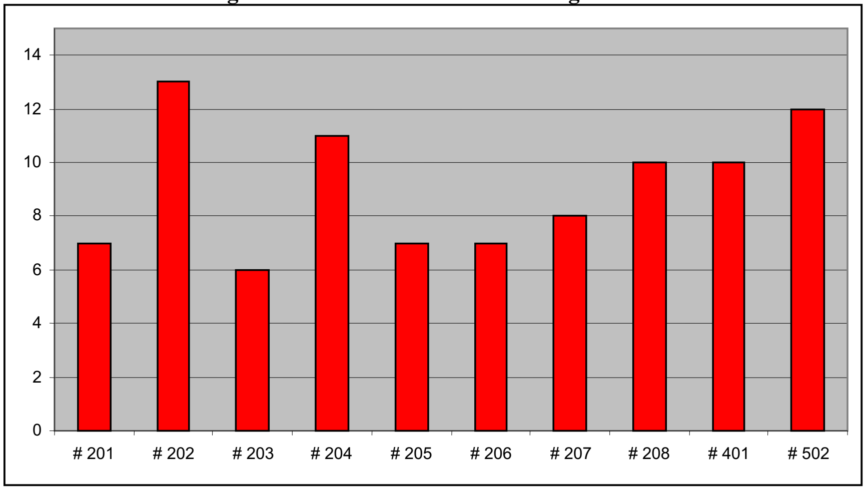
The first step in the evaluation involved testing common acrylated oligomers for basic adhesion and flexibility on the PLA substrates. In order to compare at equal print viscosity and to use a viscosity suitable for flexographic printing, the value of the lowest viscosity material (undiluted) was used as the target viscosity. In the initial investigation (Table 1), the lowest viscosity material was the amine modified polyester acrylate at 500 mPa.s @ 25°C. Trimethylolpropane Triacrylate (TMPTA) was selected as the reactive diluent since this monomer is commonly used in the graphics arts industry as it provides a good balance of viscosity control and reactivity. Differences in adhesion were observed with the same blend on the two films with adhesion being slightly inferior on the label grade film. The adhesion results reported in Table 1 is the average result from testing the blends on both films.

Table 1 - Oligomer evaluation

Acrylate Type	Relative Functionality	# 201	# 202	# 203	# 204	# 205	# 206	# 207	# 208	# 401	# 502
Amine Modified Polyester Acrylate	Mid	92									
Fatty Acid Modified Polyester Acrylate	High		35								
Bisphenol-A Epoxy Acrylate	Low			23							
Aliphatic Urethane Acrylate	Low				23						
Fatty Acid Modified Epoxy Acrylate	Low					55					
Amine Modified Epoxy Acrylate	Low						40				
Aromatic Urethane Acrylate	High							60			
Acrylic Oligomer/Monomer blend	Low								55		
Aliphatic Urethane Acrylate	Mid									46	
Epoxidized Oil Acrylate	Mid										28
Trimethylolpropane Triacrylate (TMPTA)	Mid		57	69	69	37	52	32	37	46	64
Liquid Photoinitiator Blend	N/A	8	8	8	8	8	8	8	8	8	8
		100	100	100	100	100	100	100	100	100	100
Reactivity		2	4	2	3	2	3	5	1	4	3
Adhesion		3	5	3	4	3	2	2	5	3	4
Flexibility		2	4	1	4	2	2	1	4	3	5

Results for reactivity, adhesion and flexibility were assessed on a scale of 1-5 with 1=poor and 5=excellent

Figure 1 Cumulative scores from oligomer evaluation



Given the adhesion differences observed on the films, two possible options for improved adhesion were investigated using sample #201. One approach involved wiping the film surface with a dry cloth before printing. This method resulted in significantly improved adhesion and indicated the presence of surface-active material on the film. However, this approach was not examined further since it would be difficult to implement on commercial printing equipment. The other approach was corona treating the film before printing using a hand-held corona treatment unit. Again, significant improvements in adhesion were observed. Since corona treatment is standard practice in the industry, it was decided to move forward with the bench testing without corona treatment – to identify materials with adhesion to the untreated film – and to further investigate corona treatment during the press trials.

The oligomer evaluation described above in Table 1 and the results summarized in Figure 1 identified differences in reactivity, adhesion and flexibility. Samples #202 and #502 provided encouraging results, as assessed by the combination of the three application requirements and both were selected for further work.

Blends of oligomer and monomer were prepared using the Fatty Acid Modified Polyester Acrylate as this had the highest combined score in Figure 1 (and is one of two oligomers used in further evaluation). This oligomer was blended with each monomer, a low level of cyan dispersion to aid observation and liquid photoinitiator using the guide formula in Table 2. These blends were printed with the hand-held anilox roll on the PLA substrates, cured and tested for reactivity, adhesion and flexibility. Results of these tests are listed in Table 3 and the combined score for each monomer is listed in Figure 2.

Table 2 – Guide formula

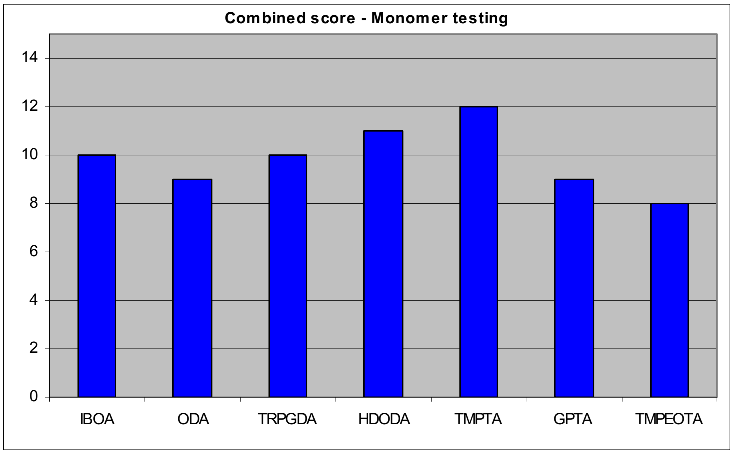
Oligomer	45
Monomer	42
Cyan dispersion	5
Liquid PI	8
	100

Table 3 – Monomer evaluation

			Reactivity	Adhesion	Flexibility
# 600	Isobornyl Acrylate	IBOA	1	4	5
#601	Octyl/Decyl Acrylate	ODA	1	3	5
#602	Tripropylene Glycol Diacrylate	TRPGDA	3	3	4
#603	1,6-Hexanediol Diacrylate	HDODA	3	5	3
#604	Trimethylopropane Triacrylate	TMPTA	5	4	3
#605	Propoxylated Glycerol Triacrylate	GPTA	5	2	2
#606	Trimethylolpropane Ethoxy Triacrylate	TMPEOTA	4	2	2

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

Figure 2 Cumulative scores from monomer evaluation



The results from the monomer evaluation indicated possible selection of four materials for use as reactive diluents. These were TMPTA, HDODA, IBOA and TRPGDA. After a review of the results, it was decided to eliminate IBOA from the list of candidates due to the high odor associated with this material, especially since the application involves a film technology intended to be "green" or "environmentally friendly." HDODA was also removed from use as a main monomer due to its tendency to attack and swell photopolymer printing plates.

However, it is anticipated that HDODA will be used at relatively low levels to boost adhesion of inks and coatings on PLA films. Therefore, the monomers chosen for further evaluation as diluents in the let-down portion were TMPTA and TRPGDA in a 1:1 ratio to combine the reactivity of TMPTA and the flexibility offered by TRPGDA.

A Low Viscosity Modified Polyester Acrylate, which was unavailable for the initial oligomer evaluations, was included at this stage as this material is intended to provide improved flow and pigment wetting in flexographic applications. The pigment dispersions (PD) listed in Table 4 were produced on a triple-roll mill and used in the ink formulations listed in Table 5.

Table 4 – Pigment Dispersions (PD)

	Yellow			Rubine			Cyan			Black		
	PD Y1	PD Y2	PD Y3	PD R1	PD R2	PD R3	PD C1	PD C2	PD C3	PD K1	PD K2	PD K3
Fatty Acid Modified Polyester Acrylate	30			30			30			30		
Epoxidized Oil Acrylate		30			30			30			30	
Low Viscosity Modified Polyester Acrylate			50			50			50			50
1:1 TMPTA:TRPGDA	30	30	10	30	30	10	30	30	10	30	30	10
Dispersing Aid	5	5	5	5	5	5	5	5	5	5	5	5
Irgalite Yellow BAW (1)	35	35	35									
Irgalite Red L4BD (1)				35	35	35						
Irgalite Blue GLO (1)							35	35	35			
Special Black 250 (2)										35	35	35
	100	100	100	100	100	100	100	100	100	100	100	100
Ease of mixing (1=GOOD/5=BAD)	1	1	1	2	2	3	1	1	1	1	1	1
Ease of milling (1=GOOD/5=BAD)	1	1	1	1	1	1	1	1	1	1	1	2
# of mill passes for < 3 NPIRI	3	3	3	8	8	9	4	3	3	6	10	6
Viscosity mPa.s @ 25C	9,110	13,700	13,000	19,900	80,600	8,300	10,400	14,600	7,310	4,080	7,590	2,940

(1) Trademarked product of Ciba Specialty Chemical
(2) Trademarked product of Degussa

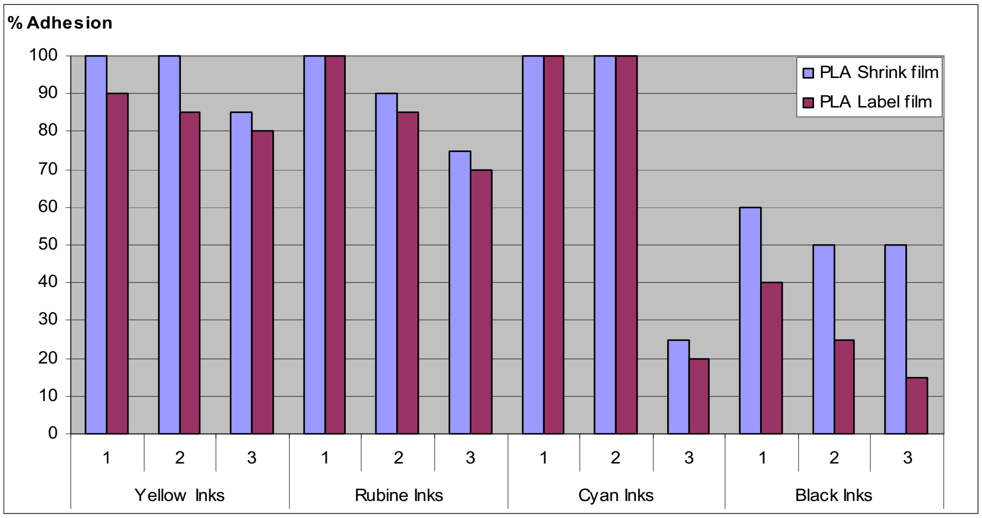
In addition to a let-down of 1:1 TMPTA and TRPGDA, epoxidized oil acrylate diluted with 1:1 TMPTA:TRPGDA was used as a let-down vehicle for those pigment dispersions based on epoxidized oil acrylate. The epoxidized oil acrylate was used in both the pigment dispersion and the ink let-down to determine if an ink made with a relatively high level of a resin manufactured from an annually renewable material would be suitable for the application.

Table 5 – Inks made with Pigment Dispersions (PD) listed in Table 4

	Yellow Inks			Rubine Inks			Cyan Inks			Black Inks		
	1	2	3	1	2	3	1	2	3	1	2	3
PD Yellow 1	50											
PD Yellow 2		50										
PD Yellow 3			50									
PD Rubine 1				50								
PD Rubine 2					50							
PD Rubine 3						50						
PD Cyan 1							50					
PD Cyan 2								50				
PD Cyan 3									50			
PD Black 1										50		
PD Black 2											50	
PD Black 3												50
Epoxidized Oil Acrylate (Diluted)		40			40			40			40	
1:1 TMPTA/TRPGDA	40		40	40		40	40		40	40		40
Liquid Photoinitiator Blend	10	10	10	10	10	10	10	10	10	10	10	10
	100	100	100	100	100	100	100	100	100	100	100	100
Viscosity mPa.s @ 25C	1050	3010	1160	390	4480	310	750	2440	630	210	1510	190

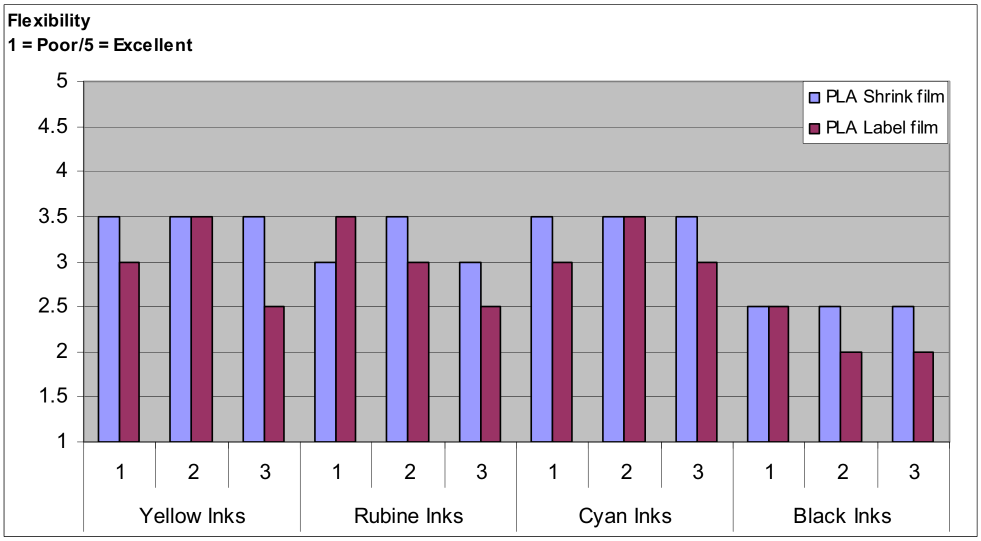
Each ink was printed with a hand-held, bladed anilox roll on the shrink grade and label grade PLA films. The prints were cured in one of Fusion's Aetek UV units with exposure measured at 120 mJ/cm^2. The cured prints were tested for adhesion, flexibility and gloss. The results are detailed in Figures 3, 4 and 5.

Figure 3 Ink adhesion



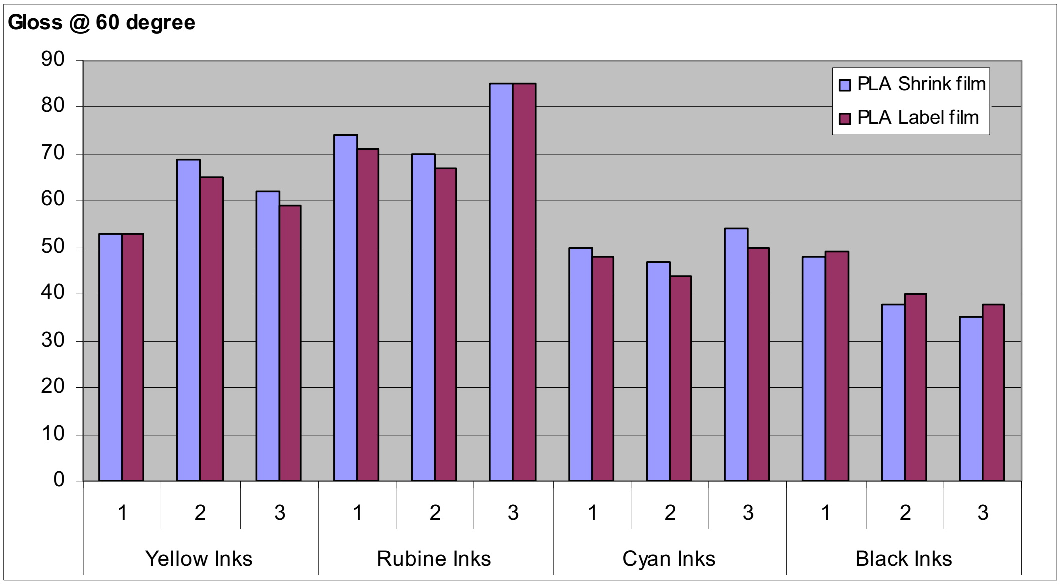
Ink adhesion was acceptable for additive-free starting formulations except for the cyan ink made with the Low Viscosity Modified Polyester Acrylate and all three black inks. Black inks are typically difficult to cure and often require specific photoinitiator blends for acceptable performance. In this evaluation, a standard photoinitiator was used at a single line speed and reactivity was not optimized.

Figure 4 Ink flexibility



Ink flexibility testing identified differences between inks and also between films. The main trend appeared to be reduced flexibility on PLA label film when compared to a print of the same ink on PLA shrink film.

Figure 5 Ink gloss



The gloss results did not identify anomalies and no significant trend emerged from the analysis. Each ink provided similar gloss results on both films.

Based on the results from the bench testing of the inks, formulations containing the Fatty Acid Modified Polyester Acrylate and the Epoxidized Oil Acrylate, each combined with the 1:1 blend of TMPTA:TRPGDA, were selected for evaluation in cyan ink on an Aquaflex brand flexographic press. Cyan was selected for press evaluation because the cyan formulations showed excellent tape adhesion on both films during bench evaluation – Figure 3. Another reason for continuing evaluations with epoxidized oil acrylate in both the pigment dispersion and the let-down was to continue to investigate the use of a relatively high level of a resin manufactured from an annually renewable material on the bio-based films.

Press performance was generally good for both ink formulations, with good lay and leveling observed. As a general overview, ink adhesion to the PLA label film was inferior to ink adhesion to the PLA shrink film. With both films, higher line speeds resulted in decreased tape adhesion, possibly due to a combination of reduced cure/reactivity of the ink and a film surface not optimized for ink receptivity. With in-line corona treatment, the adhesion improved significantly on both films even at line speeds where ink adhesion was previously unacceptable. However, in several instances 100% ink adhesion was not achieved even with corona treatment. One possible reason for this lack of perfect adhesion may be that the starting point formulations did not contain additives and/or oligomers used to enhance ink adhesion on non-porous substrates.

In several tests with the print samples from the press trial, adhesion appeared to differ from one side of the roll to the other i.e. across the web. This was observed with both the PLA Label film and the PLA Shrink film although the variation was more obvious with the PLA label film. The reported adhesion results are averages of the ink adhesion as tested in several areas across the web. Figures 6, 7, 8 and 9 represent the results from the press trials.

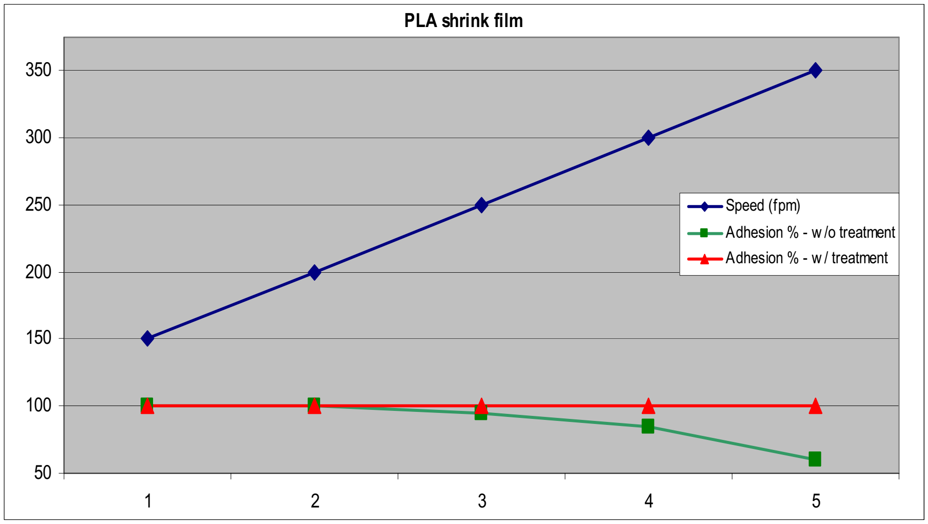


Figure 6 Fatty Acid Modified Polyester Acrylate-based ink on PLA shrink film with & without corona treatment

The results with PLA shrink film outlined in Figure 6 indicate a correlation between corona treatment and increased tape adhesion of the UV Blue ink. At relatively low line speed, the ink had very good adhesion with and without corona treatment. However, as line speed was increased, a significant decrease in adhesion was observed without corona treatment. The line speed was maintained, the corona treatment was turned on and the adhesion of the ink to the substrate was significantly improved.

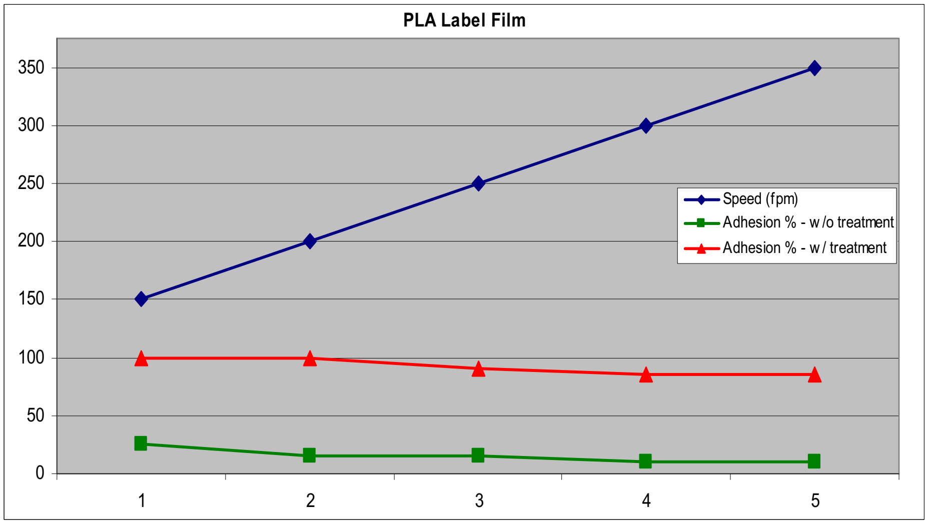


Figure 7 Fatty Acid Modified Polyester Acrylate-based ink on PLA label film with & without corona treatment

The results in Figure 7 with the Fatty Acid Modified Polyester Acrylate-based blue ink on PLA label film show poor tape adhesion without corona treatment. With corona treatment, adhesion was significantly increased but 100% tape adhesion was not achieved at higher line speeds.

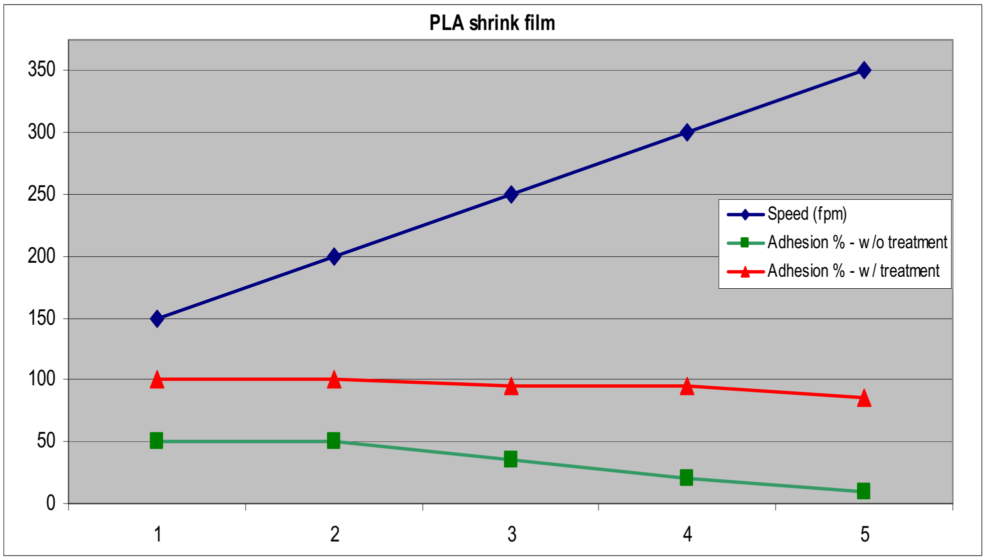


Figure 8 Epoxidized Oil Acrylate-based ink on PLA shrink film with & without corona treatment

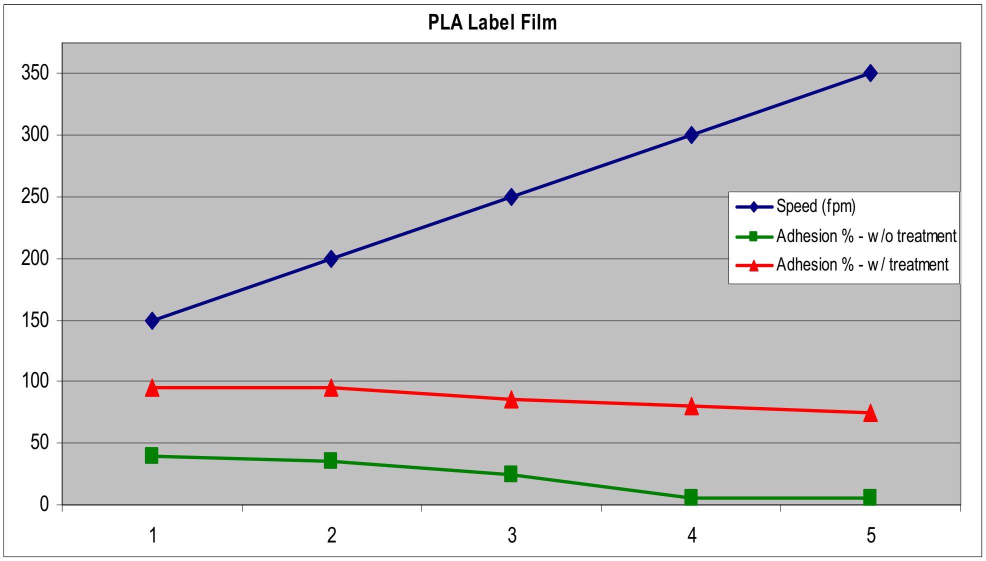


Figure 9 Epoxidized Oil Acrylate -based ink on PLA label film with & without corona treatment

The results in Figures 8 and 9 with Epoxidized Oil Acrylate-based blue ink show poor tape adhesion without corona treatment coupled with inferior results on PLA label film. With corona treatment, adhesion increased significantly on both films, but 100% tape adhesion was not achieved at higher line speeds. In this evaluation, a high oligomer level was used to maintain a “green” approach in combination with PLA film while maintaining flexo-type viscosity. However, adjustment will be required to find the best compromise between tape adhesion and environmental considerations.

Conclusions

While formula modifications will be necessary to meet specific application, converting and end-use requirements, the results from the evaluations confirmed suitability of UV flexographic inks on commercially available PLA shrink and label films. As energy-cure inks and coatings are developed for use on PLA films for flexible packaging, the following results and observations from this study may be considered to accelerate product delivery:

1. Surface “activation” either by wiping or corona treatment significantly improved ink adhesion on both films. After in-line corona treatment and printing on press, PLA shrink film exhibited better adhesion than PLA label film.
2. Fatty Acid Modified Polyester Acrylate-based ink displayed better adhesion than the Epoxidized Oil Acrylate-based ink. Therefore, if the “green” property is desired in both film and ink, optimization of the level of Epoxidized Oil Acrylate will be required to find the best balance of properties.
3. The level 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.
4. A more detailed investigation into the reasons for erratic adhesion from one side of the roll to the other, i.e. across the web, should be completed.

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