UV LED Low Migration Laminating Adhesives for Flexible Packaging

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The global flexible packaging market continues to evolve as shifts in consumer preference lean more toward convenience in single serve or grab-n-go options, extended shelf life, and sustainability. In addition to consumers driving innovation in flexible packaging, participation of wide web and now narrow web converters are beginning to converge into the packaging space as they see increased opportunity in equipment and coating technologies, thereby lowering the barrier-to-entry. With the advancements of UV LED (ultraviolet light emitting diodes) curing technology, opportunities in the flexible packaging space become more available to the converter base.

Flexographic Packaging Market Trends

According to Smithers Pira, the global flexographic printing industry is forecasted to reach $980 billion by 2018, primarily driven by growth in packaging and labels. With over 15,000 label converters and almost 500 flexible packaging converters globally, operating multiple press technologies in multiple plants, there is growing M&A activity that is converging the two market segments, convoluting the packaging space while strengthening a converter's position. With the label market slated to grow only 2% annually and flexible packaging at a strong 5%, there is even more reason for a company to acquire adjacent technologies or competitors to complement their business strategy.

Many drivers are attributed to the growth in the flexographic packaging market including consumer preferences (particularly from millennials, who desire convenience and single serve packaging), the need for increased shelf life, pet food manufacturers moving away from multiwall bags to flexible packaging and growing interest in moving away from rigid to flexible structures.

Flexographic Market Segments

The flexographic market segments can be divided into three primary categories: narrow web, mid web and wide web with each defined in Table 1. Note: the widths defining each market segment are a general specification and not stated industry standard.

Table 1 – Flexographic Market Segments

Segment	Width	Press Type	Formulations	Applications
Narrow Web	< 30" < 800mm	In Line Flexography	Mostly UV Water, solvent, and solvent-free	Tag and Label
Mid Web	30 to 60" 800 to 1600mm	Central Impression (CI) Stack Gravure	Water, solvent, and solvent-free Some UV coatings	Flexible Packaging (short runs)
Wide Web	> 60" > 1600mm	Central Impression (CI) Gravure	Water, solvent, and solvent- free Some UV coatings	Flexible Packaging (large runs)

Due to the significant growth in flexographic flexible packaging, the limitations of traditional UV curing technologies that currently prohibit label and flexible packaging converters from participating in this segment has been exposed. Particularly in the food and beverage segment which is > 50% of the overall flexible packaging market. One way to eliminate the barrier-to-entry is to fully understand the benefits of UV LED technology and the value it brings to the flexible packaging market.

Types of UV LED Flexographic Formulations and Technologies

Inks, coatings, and adhesives formulated for cure with UV LED are increasingly gaining traction in the narrow, mid, and wide web markets. While some formulations such as silicone-release and highly functional coatings with smaller overall market demand have seen limited UV LED development, the broader portfolio of UV LED formulated inks, coatings, and adhesives already exist commercially for a wide range of converter requirements. In situations where off-the-shelf formulations are not the best match for a particular application, the existing formulation can typically be modified to fit the converter's specific processing, construction, or application needs. As a result, generalized claims that most UV LED formulations do not exist is misleading and detracts from the primary focus which should be on the tremendous operational and economic benefits associated with UV LED curing.

The greatest commercial use today at press speeds of up to 1,000 fpm are UV LED formulated line, process, and high density inks in both general purpose and low migration formulations. Metallic and fluorescent UV LED variations are also being adopted by converters since the use of UV LED curing sources results in a truer and brighter cured metallic and fluorescent look. In addition, fluorescents have been shown to fade much less when passed under multiple UV LED lamps on a press than with a similar number of passes under conventional mercury lamps. Recent formulation improvements in clear UV LED primers, laminating adhesives, and over-protective varnishes are now enabling non-yellowing in the final cure at ever increasing press speeds that are quickly approaching those of UV LED cured inks.

Advantages of UV LED Curing

While new narrow web presses are sometimes sold with hot air driers for water based and solvent based formulations, the vast majority are equipped with UV driers. This is due to the many operational and final product advantages that UV curing offers converters and brands. Refer to Figure 1.

For the mid and wide web flexo, gravure, and coating market segments, presses are generally built to run water based, solvent based, or solvent-less inks, coatings, and adhesives. Converters will often run a UV cured silicone release coating in nitrogen, a UV cured over protective varnish, or a laminating adhesive in combination with these formulations. This is commonly done off-line or at a specified distance from the solvent formulations in order to comply with appropriate explosion proofing requirements. It is important to note that due to the electrical design of UV LED sources and their compactness, UV LED curing offers the potential to convert many of these mid and wide web applications to UV and even run UV LED technology in-line with solvent formulations.

Regardless of the web width or press configuration, UV LED curing offers all the advantages associated with conventional mercury lamps as well as a long list of additional environmental, operational, and performance benefits only possible with UV LED systems. Refer again to Table 2.

Table 2 – Advantages of UV Curing

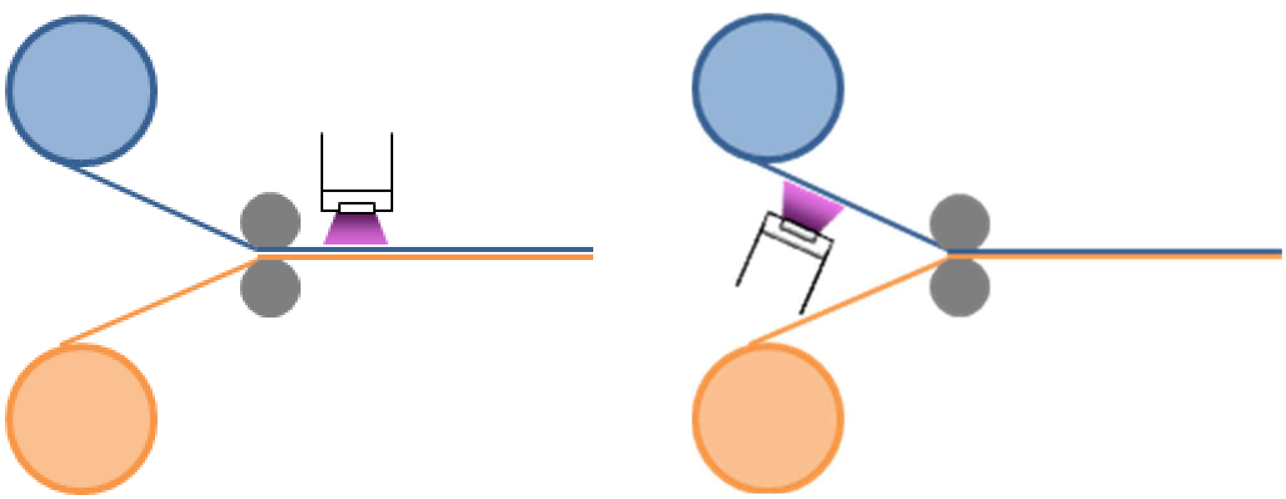
Benefits of Conventional Mercury and UV LED	Additional Benefits of UV LED
Viable with Inks, coatings, and adhesives	**Long source life (+20K hours)**
100% solids formulations	**Marginal UV degradation over life**
Brighter and bolder colors	**Superior cured whites, metallics, and fluorescents**
Scratch, water, and chemical resistance	**Instant On/Off (no shutters)**
Fast and complete cure	**50% lower energy consumption**
No volatile organic compounds in exhaust	**Reduces heat transfer to media**
Eliminates racking or thermal oven	**More compact heads with solid state technology**
Increases production speeds	**Further increases production speeds**
Reduces needed floor space	**Further reduces needed floor space**
Reduces reject rates	**Improves overall process control**
Reduces waste	**No mercury filled bulbs**
Superior adhesion to media	**No ozone or exhaust**
Formulations can be left in press	**Better adhesion and through cure**
Long pot life	**Lower maintenance**

Description of UV LED Laminating Process

In flexible packaging applications, the process of laminating is used to securely bond two or more flexible constructions such as PET, PE, PP, paper, and foil among others. The two constructions are unwound on press from their respective rolls. The laminating adhesive is applied to the substrate with lower absorption properties before being nipped or pressed to the second substrate. Formulation application methods include flexo, gravure, and coaters. The two substrates combined with the wet adhesive sandwiched between both layers are then passed underneath the UV LED source for immediate cure. Refer to Figure 1. PSAs, on the other hand, are dry cured since the first construction and PSA are passed under the UV light before being pressed to the second construction.

Since UV LED has the advantage of transferring less heat to the pouch structures, it expands the range of substrate gauges that can be used in an application. It should be noted, this is not a cold cure technology as UV LED wavelengths are still a form of energy. UV LED basically results in less energy being converted to heat at the substrate surface when compared to other curing sources. For some incredibly heat sensitive substrates, it is helpful to cure on the outside surface of a chilled drum or roller as a means of managing better substrate and process control, but it is not always necessary.

Figure 1 - a) UV LED Laminating Adhesive Press Set-up and b) UV LED PSA Press Set-up



UV LED Laminating Adhesive Press Set-Up **UV LED PSA Press Set-up**

UV LED Laminating Adhesives vs Traditional UV Laminating Adhesives

In determining the potential value proposition of UV LED versus traditional UV mercury technology, one should look to the higher performance of the laminating adhesives in conjunction with UV LED curing technology. With UV LED, the corresponding laminating adhesive provides a longer pot life and immediate cure, as compared to solvent free laminating adhesives which may take up to five days to fully cure. With the benefit of immediate cure, flexible packaging rolls can be slit and pouched immediately offering the converter short runs and quick turns to their customers. As well, UV LED laminating adhesives can be applied with existing flexographic or gravure cylinders, and UV LED stations can easily be retrofitted onto existing equipment which equals lower total capital investment.

Low Migration Regulatory Compliance for Flexible Packaging

In complying with regulations in food safety, particularly when introducing UV LED laminating adhesives, utilization of the appropriate regulatory agency (FDA, EFSA) guidelines for migration and risk assessment is critical. For the US, relying on the FDA's Toxicology and Chemistry guidelines is the most logical starting point. Following these guidelines in developing the needed migration protocol that simulates the foods and conditions of use for food packaging in addition to determining the risk of exposure to chemical migrants will protect converters from potential legal implications.

There are three areas that must be understood in order to evaluate safety in food packaging applications. Refer to Table 3.

First, it is necessary to understand the types of foods and ingredients that are going to be packaged. Below are the most common flexible packaging structures matched to typical end use applications and their corresponding adhesive laminating technology.

Table 3 – Most Common Flexible Packaging Structures

Laminating Adhesive Technology	Typical Constructions	Typical End Uses
Solvent Free	PET/PE OPP/PE OPP/OPP	Confectionary bags
	OPA/PE	Meat & cheese lidding
	CPA/PE	Base thermoforming webs for vacuum packs of meats & cheese
	PET/Alu/PE	Instant & ground coffee Dried soups & sauces
	MPET/PE	Ketchup, ground coffee
Solvent Based	CPA/PE	Base thermoforming webs for vacuum packs of meats & cheese
	PET/Alu/PE	Instant & ground coffee Dried soups & sauces
	MPET/PE	Ketchup, ground coffee
	PE/MPET/PE	Bag-in-box wine, fruit pulp, tomato paste
	PET/Alu/CPP	Retort wet pet food
	PET/Alu/OPA/CPP	Retort liquid soups & sauces
	PET AlOx or SIOx/OPA/CPP	Microwavable retort rice, ready meals
	Alu/OPA/PVC	Lidding for pharma blister
Water Based	Paper/MPET/HS Coating	Yogurt Lidding
Hot Melt PSA	PET/PE	Reclosure lidding for deli meats & cheeses

Secondly, once the application and the type of food that is being packaged have been identified, using the FDA's Toxicology and Chemistry Guidelines (Refer to Table 4), it is necessary to determine the recommended simulants that will need to be used in condition testing to determine the migratory properties of the structure.

Table 4 – FDA's Toxicology and Chemistry Guidelines

Aqueous & Acidic Foods	Alcoholic Foods	Fatty Foods	Dry foods
Fruits, vegetables, juices, mustard, ketchup, salad, milk, bread	Beer, ale, wine, distilled spirits	Cheese, butter, meats, seafood, ice cream, doughnuts, cookies, potato chips, nuts	Uncooked pasta, cereals, rice cakes, coffee (non-flavored)
			
10% ethanol/ 90% water Note: 3% acetic acid should only be used when food acidity is expected to lead to significantly higher levels of migration than with 10% ethanol.	**10% ethanol/ 90% water** (unless amount of alcohol in final package is >10%, then use actual ethanol wt%)	**95% ethanol/ 5% water (or oil simulant)** Note: Fatty foods represent the majority of the solvent-free laminating adhesive market and have the most challenging simulant standards	**Not specified**

www.fda.gov/Food/IngredientsPackagingLabeling/PackagingFCS/default.htm

Lastly, consider the conditions of use the pouch will be subjected during the processing phase. Using the FDA conditions, testing must be completed per the appropriate condition for the required application.

According to the FDA, the various conditions from A-J to be potentially tested are:

A. High temperature, heat sterilized or retorted (ca. 121ºC (250ºF))
B. Boiling water sterilized (100ºC)
C. Hot filled or pasteurized above 66 ºC (150ºF)
D. Hot filled or pasteurized below 66 ºC (150ºF)
E. Room temperature filled and stored (no thermal treatment in the container)
F. Refrigerated storage (no thermal treatment in the container)
G. Frozen storage (no thermal treatment in the container)
H. Frozen or refrigerated storage: ready prepared foods intended to be reheated in container at time of use
I. Irradiation (ionizing radiation)
J. Cooking at temperatures exceeding 121ºC (250ºF)

Another key aspect to consider when evaluating the structure is the type of functional barrier being used. The functional barrier prevents a varying degree of migration of the non-food contact material in what is being pouched; particularly if the contents are food. However, there is very little guidance from the FDA or EU that defines performance of an adequate functional barrier and its corresponding acceptable migration levels. Ultimately, it is the converter and contract packager's responsibility to determine the needed functional barrier. When testing the structure compliance of the package, ensure the hazard information of the migrants and safe dietary levels are reviewed. Using the FDA default exposure values, determine the exposure level of the package such as percent of diet exposed to the packaging type. This can be calculated by dividing the safe dietary level by the exposure where a detection limit can be derived.

$$\text{Detection Limit} = \frac{\text{Safe Dietary Level}}{\text{Exposure}}$$

The same FDA regulatory requirements that apply to today's packaging standards are also applicable when transitioning from a traditional laminating adhesive such as solvent free to UV LED. As long as the appropriate steps are taken in the risk assessment of the packaging including component migration, toxicological data established limits, and performing tests in all applicable food types, temperatures and conditions, UV LED technology is a viable, efficient and green method of cure. Furthermore, UV LED technology has the advantage of providing a curing process that is reliable, repeatable, and extremely controllable. With low migration and regulatory compliance, it is critical that process variables are monitored and kept within the defined operating window. UV LED technology coupled with UV LED formulated laminating adhesives for low migration applications are an innovative and sustainable technological trend that will have growing importance in flexible packaging for those early adopters in the narrow, mid and wide web space that are searching for market differentiation.

Experimental

Laminations were made on the Mark Andy P5 press at Flint's facility in Rogers, MN (refer to Figure 2) with a Mark Andy Gen 2 ProLED (Phoseon FP601), 20 W/cm², 395 nm, flat glass emitting window, UV LED curing station. The flexographic anilox for applying the adhesive was 360 lpi/5.42 bcm. MP 2 mil PE was the base, and MP 75 gauge PP was the overlaminate. The laminating adhesives tested were Ashland Adhesive 1 and Adhesive 2. The press was run up to 500 fpm, and at LED power settings ranging from 25-100%. Neither adhesive displayed any yellowing. The best adhesive bonds for this construction were achieved by Adhesive 1 so these laminations were chosen for migration testing. Initial hand peels resulted in destruct bonds up to 500 fpm at 25% power. The migration testing was conducted by placing the laminations in specially designed aluminum and glass cells (refer to Figure 3) with the food contact side of the construction exposed to the food simulant. The food simulant was 95% ethanol to cover fatty food types, and 10 mL/in² was applied as the default amount. Condition of Use C (hot fill above 150°F) was tested by holding the food simulant in the cells at 66°C for 2 hours, followed by 10 days at 40°C. HPLC-MS analysis was performed to detect any components of the adhesive in the food simulant, and the data was reviewed by a food packaging toxicologist who performed a risk assessment. A safe threshold of 50 ppb was set by taking into account toxicological data and daily consumption factor of 1% used in FCN 642. The data is presented in Table 5. These results indicated that the samples made at up to 300 fpm are safe for use in food packaging. The laminations made at 500 fpm had migration of both monomers above the limit.

Figure 2 – Flint's MA P5 Press

Figure 3 – Migration Cells

Table 5 – Migration Data from Flint trial

		1% CF (ppb)		
Sample Label	**Press Speed/100% UV LED Power**	**Monomer 1**	**Monomer 2**	**Photoinitiator 1**
C-1	Control	ND	ND	ND
C-2	Control	ND	ND	ND
C-3	Control	Sample lost during extraction testing		
S4-1	100 fpm	29	38	3
S4-2	100 fpm	27	33	2
S4-3	100 fpm	26	34	2
S5-1	300 fpm	45	47	7
S5-2	300 fpm	41	42	6
S5-3	300 fpm	38	41	6
S6-1	500 fpm	75	79	12
S6-2	500 fpm	Sample lost during extraction testing		
S6-3	500 fpm	54	52	8

A second round of laminations were made in the Ashland lab in Dublin, OH. A Harper flexographic hand proofer with a 260 lpi/5.48 bcm anilox was used for applying the adhesive to the samples, and they were cured with an American UV fitted with a Heraeus 16 W/cm², 395 nm, UV LED at 100% power. MP 3 mil PE was the base, and MP 75 gauge PP was the overlaminate. The laminating adhesive tested was Ashland Adhesive 1. The conveyor belt was run up to 500 fpm. The migration testing was conducted by placing the laminations in specially designed aluminum and glass cells (refer to Figure 3) with the food contact side of the construction exposed to the food simulant. Three conditions were tested. The food simulants were 95% ethanol to cover fatty food types and 10% ethanol to cover aqueous food types. 10 mL/in² was applied as the default amount. Condition of Use C (hot fill above 150°F) was tested by holding the food simulant in the cells at 66°C for 2 hours, followed by 10 days at 40°C. Condition of Use E (room temperature fill and storage with no thermal treatment) was tested by holding the food simulant in the cells at 40°C for 10 days. HPLC-MS analysis was performed to detect any components of the adhesive in the food simulant, and the data was reviewed by a food packaging toxicologist who performed a risk assessment. A safe threshold of 50 ppb was set by taking into account toxicological data and daily consumption factor of 1% used in FCN 642. The data is presented in Table 6. These results indicated that all the samples are safe for use in food packaging.

Table 6 – Migration Data from Ashland Lab Samples

	1% CF (ppb)		
A: 95 % EtOH/ Condition of Use E	**Mono. 1**	**Mono. 2**	**PI 1**
A-1: 100FPM	10	17	3
A-2: 100FPM	10	18	3
A-3: 100FPM	11	21	3
A-4: 300FPM	12	20	8
A-5: 300FPM	11	19	8
A-6: 300FPM	10	19	8
A-7: 500FPM	17	27	10
A-8: 500FPM	17	27	9
A-9: 500FPM	16	24	9
A-10: control	< DL	< DL	ND
A-11: control	< DL	< DL	ND
A-12: control	< DL	< DL	ND

	1% CF (ppb)		
B: 10 % EtOH/ Condition of Use E	**Mono. 1**	**Mono. 2**	**PI 1**
B-1: 100FPM	6	14	2
B-2: 100FPM	5	12	2
B-3: 100FPM	5	12	2
B-4: 300FPM	6	16	6
B-5: 300FPM	5	15	6
B-6: 300FPM	5	15	6
B-7: 500FPM	8	17	7
B-8: 500FPM	7	15	6
B-9: 500FPM	6	14	5
B-10: control	< DL	< DL	ND
B-11: control	< DL	< DL	ND
B-12: control	< DL	< DL	ND

	1% CF (ppb)		
C: 10 % EtOH/ Condition of Use C	**Mono. 1**	**Mono. 2**	**PI 1**
C-1: 100FPM	9	20	3
C-2: 100FPM	8	19	3
C-3: 100FPM	7	17	2
C-4: 300FPM	10	25	7
C-5: 300FPM	9	25	7
C-6: 300FPM	10	26	7
C-7: 500FPM	14	30	7
C-8: 500FPM	17	31	7
C-9: 500FPM	Sample lost		
C-10: control	< DL	< DL	ND
C-11: control	< DL	< DL	ND
C-12: control	< DL	< DL	ND

Conclusion

Under the right conditions of adhesive chemistry, degree of cure, laminate construction, food type and condition of use, UV LED laminating adhesives are safe for use in flexible food packaging. It is important for converters to confirm the safety of the adhesive in their flexible packaging. This can be achieved by careful adhesive selection and control of their manufacturing practices. Suppliers of UV LED curing stations and laminating adhesives can assist in this process.