Waterbased UV LED Curable Compositions for Graphics Applications, Including Food Packaging and Inkjet Inks

Jo Ann Arceneaux, Tong Wang, Hwei-Ling Yau
allnex USA Inc.
Alpharetta, GA USA

Michel Tielemans, Kevin Poelmans, Laurence Boutreau
allnex Belgium SA/NV
Drogenbos, Belgium

ABSTRACT

With the increasing regulatory pressure on acrylate monomers, the energy curable graphics market has started to investigate the use of energy curable waterborne resins and polyurethane dispersions (PUDs). These products can be designed to provide high reactivity, and cured inks and coatings with superior mechanical and chemical resistance and excellent adhesion to plastics. Some products are particularly suitable for food contact applications as illustrated by comprehensive migration tests and compliance with existing regulations. These energy curable waterborne resins and PUDs also find utility in the development of next generation low viscosity inkjet inks and overprint varnishes where re-dispersibility in water is required. Data on the performance of these waterborne systems cured with both mercury lamps and LED lamps will be presented.

INKJET INK TECHNOLOGIES

Today, inkjet inks are either solventborne, waterborne, or 100% solids energy curable. Solventborne (SB) and waterborne (WB) inkjet inks are based on polymers, colorants, and additives dissolved/dispersed in either solvent or water. These are well known technologies, with a large installed equipment base. They are generally slow curing with low resolution and color strength. The resistance properties of the cured inks are also rather poor. The solventborne inks have good adhesion to substrates, but due to VOCs, are not environmentally friendly. Waterborne inks can have adhesion issues on non-porous substrates, and also contain emulsifiers and coalescents, which contribute to VOC. Both of these technologies can dry in the print heads causing blocked nozzles.

The 100% solids energy curable (EC) inkjet inks are very fast curing with improved resolution and color strength. They have better resistance properties, and are low VOC. However, some of the more opaque inks are difficult to cure because of film thickness. These EC inkjet inks are based on acrylated oligomers and monomers, pigments, additives, and photoinitiators. They must contain high levels of acrylated monomers to reduce viscosity, and more of the monomer is mono-functional due to the very low viscosity requirements. This monomer use results in odor and safety concerns, and in many cases, the GHS labeling is not user friendly. The photoinitiator (PI) and its fragments may also create concerns for food packaging applications. (If electron beam (EB) cure is used, no PI is necessary, and this concern is eliminated.) Energy curable inkjet inks do not dry in the print heads, so nozzle blockage is not a concern.

Waterbased energy curable inkjet inks combine the benefits of both waterbased and energy curable inks, and eliminate many of the drawbacks. These types of inkjet inks maintain the fast cure, good resolution, color strength, and resistance properties of 100% solids EC inkjet inks, and have low VOC (no solvent, emulsifiers, or coalescents). They also eliminate the use of low molecular weight monomers, resulting in lower odor and easing of regulatory and environmental concerns. The inkjet printed product has lower dry film thickness, allowing better cure of opaque inks (but this can still be a problem), and providing a better hand or feel. This product is also very durable and has better adhesion to plastics due to lower shrinkage. Waterbased energy curable inkjet inks also separate the drying step from the curing step and are resoluble, so these types of inks do not block the nozzles. Thus, the value proposition for EC waterbased inkjet inks is 100% solids EC performance, with improved processability and VOCs over WB and SB inks, and improved safety over 100% solids EC inks. Table 1 summarizes the benefits and drawbacks of the inkjet ink technologies.

The EC waterbased inkjet ink value proposition opens the door to food packaging applications. Food packaging applications require global regulatory compliance (EuPIA, Nestle List, Swiss List, German Ordinance, FDA, REACH, Prop 65,…), no use of chemicals of concern, no/low residuals, extractables, or migrating species, no/low odor, and no/low VOC. The EC waterbased inkjet inks based on polyurethane dispersions (PUDs) can be designed to meet these requirements.

Table 1. Benefits and Drawbacks of Inkjet Ink Technologies

	Waterborne	Solventborne	100% Solids EC	Waterborne EC
COMPONENTS	Polymers, Colorants, Additives, Water	Polymers, Colorants, Additives, Solvent	Oligomers, Pigments, Additives, Monomers, (PI)	EC PUDs, Pigments, Additives, (PI)
BENEFITS	Known Chemistry	Known Chemistry	Fast Cure	Fast Cure
	Installed Base	Installed Base	Durability	Durability
		Adhesion	Resolution	Resolution
			Color Strength	Color Strength
			Low VOC	Low VOC
DRAWBACKS	Speed	Speed	Cure of Opaque Inks	Cure of Opaque Inks
	Resolution	Resolution	Residual Monomers	
	Color Strength	Color Strength	PI Fragments (UV only)	PI fragments (UV only)
		VOC	Odor	

DESIGN OF ENERGY CURABLE PUDs

A cartoon of an energy curable PUD is shown in Figure 1. The composition of the EC PUD can be varied to provide for different properties. As shown in Table 2, EC PUDs can be designed to be label free (GHS) and BPA free. Tackiness and resolubility after dry but before cure are two properties that can also be controlled. Other parameters, such as migration potential, reactivity, and flexibility can also be varied. Although not shown in Figure 2, adhesion properties can also be designed into the EC PUD.

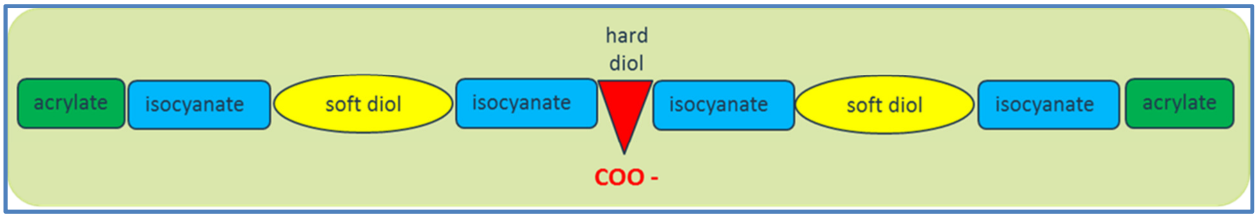


Figure 1. Cartoon of an Energy Curable Polyurethane Dispersion

Table 2. Properties of EC PUDs

	Label-free	BPA-free	Tack-free	Resolu-bility	Migration	Reactivity	Flexibility
First Generation Products							
EC PUD 1	● green	● green	● red	● green	● yellow	● yellow	● green
EC PUD 2	● green	● green	● red	● green	● yellow	● yellow	● green
EC PUD 3	● green	● red	● yellow	● green	● yellow	● yellow	● green
Developmental Products for Low Migration							
EC PUD 912	● green	● green	● green	● red	● green ● yellow	● yellow	● green
EC PUD 929	● red	● green	● green	● green	● green	● green	● yellow
EC PUD 953	● red	● green	● red	● green	● green	● yellow	● green
● green Recommended Use	● yellow Fair Use	● red Not Recommended					

WATERBASED ENERGY CURABLE PUDs FOR FOOD PACKAGING

The composition of the EC PUD can also be designed to provide properties necessary for food packaging inkjet inks. Some of these properties are listed below:

1. Low viscosity without the use of solvent or monomers
2. High molecular weight to avoid extraction/migration; no low molecular weight (< 500) fractions (However, EC PUDs are lower MW than traditional PUDs.)
3. High functionality (>/= 6) to provide dense crosslinking and high performance
4. Controlled composition for other desirable properties such as stability, resolubility, and adhesion

The starting raw materials must also be controlled to avoid the use of chemicals of concern, such as tin, bisphenol A, alkyl phenol ethoxylates (APEO), and others. Figure 2 provides compositional data on EC PUD 929. This product contains greater than 99.5% (solids) of material with MW > 500 Daltons *and* functionality >/= 6, indicating its suitability for use in food packaging. (Mn = 1,875, Mw = 27,600, and Mw/Mn = 14.68.)

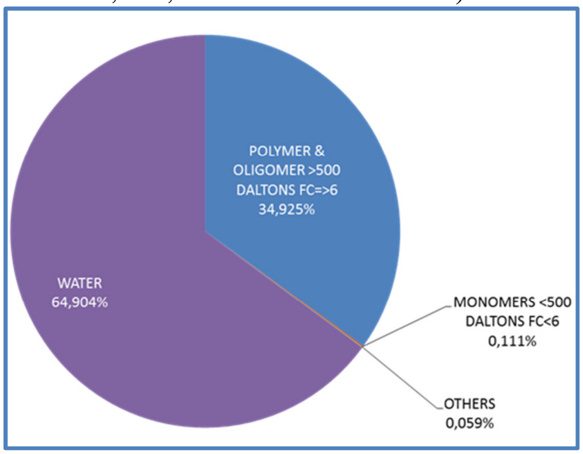


Figure 2. Composition of EC PUD 929

Validation of the suitability of the EC PUD for use in food packaging should include migration tests and identification of extractables. These tests were performed on EC PUD 929 and two reference EC PUDs that were not specifically designed for food packaging applications. A *direct* food contact protocol was used to address the most stringent extraction conditions. The polymer dispersions were formulated with a wetting agent (0 – 0.75%) and applied as a 30µ wet coating on an unwashed aluminum sheet. They were dried for 4 minutes at 60°C, and then cured with an electron beam (250 keV - 5 MRad) with a conveyer speed of 10 m/min. The coated samples were immersed in 95% ethanol for 24 hours at 60°C in a closed glass flask. There was a contact area of 100 ml of solvent per dm^2 of coated substrate. (These extraction conditions are related to FDA § 176.170 – conditions of use H, for paper and paperboard in contact with aqueous and fatty foods.)

The alcoholic solution was submitted to GC-MS and LC-MS after collecting reference data from the pure polymer dispersions. Extractable components were identified and detected at suspected ppb levels by single ion monitoring (SIM). The MS response was recorded as peak areas for a comparative analysis, without considering that the MS response factors are different for each type of products. The extraction data from the two analytical techniques were merged and normalized so that they could be categorized per product type. As shown in Figure 3, EC PUD 929 shows very favorable migration data versus the non-food grade EC PUDs, References 1 and 2. Based on these data, EC PUD 929 should be acceptable for indirect food packaging applications.

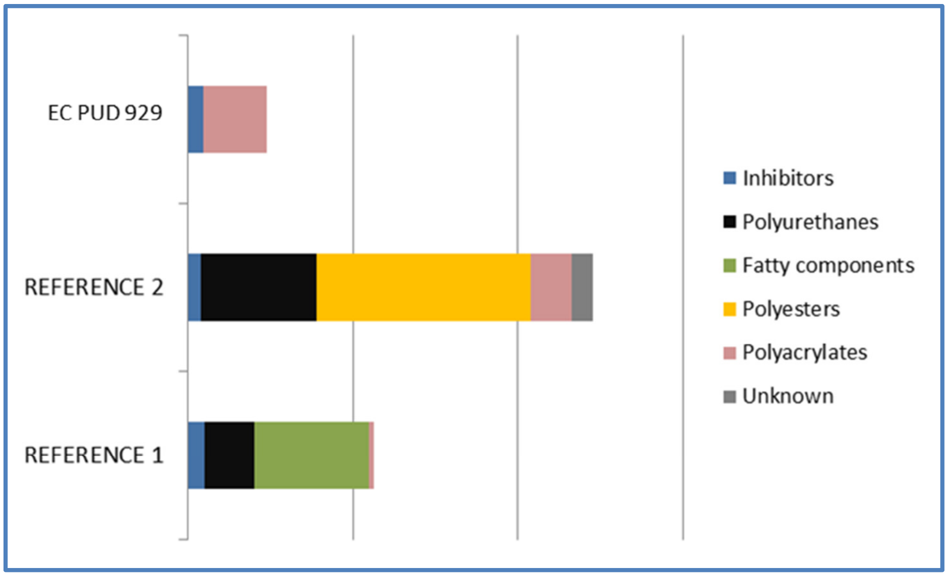


Figure 3. Extractables at Suspected ppb Levels from Direct Food Contact Protocol

ENERGY CURABLE INKJET INK REQUIREMENTS

There are two major inkjet application techniques, continuous and drop-on-demand. Drop-on-demand is further divided into piezo and thermal (bubble jet) technologies. The 100% solids energy curable inkjet inks are typically applied through piezo technology. Because of viscosity constraints, the 100% solids inkjet ink is generally heated to 40°- 60°C before jetting. EC waterborne inkjet inks could be jetted by either piezo or thermal technologies.

There are many requirements of an EC waterbased inkjet ink, and some of these follow. The inkjet ink must be stable, both during application and during storage. An elevated temperature stability test over a set period of time is the typical test (45-60°C over various time periods). This accelerated aging test is used to predict room temperature shelf life of the inkjet ink. Viscosity, pH, particle size, and/or coagulum are monitored during this test. The inkjet ink must be efficiently filterable to remove particles that may block or damage the inkjet head.

The inkjet ink must be jettable using whichever inkjet head is specified. Jettability is typically a function of surface tension, rheology, and solids content. The inkjet ink must be resoluble before cure to avoid clogging the inkjet nozzles. Finally, the inkjet ink must be reactive or curable under the lamp and speed conditions of the specified press, and the cured ink must provide the adhesion and resistance properties required by the end application. These requirements will be further explained and discussed.

INK STABILITY

Figure 4 shows the results of a stability test of EC PUD 929 held for 9-10 days at 60°C. The EC PUD 929 was diluted to 10% solids for this test. The particle size of EC PUD 929 decreased only slightly over 9 days (80 nm to 75 nm). Over a 10 day period, there was a decrease in pH from 7.9 to 7.1, and in viscosity from 1.9 to 1.5 cP at 25°C. All of these results indicate a stable system. CMYK (Cyan, Magenta, Yellow, Black) inkjet inks were also evaluated for stability over time at 50° C. Figure 5 shows the viscosity evolution in cP of these inks at 0, 2, 4, and 6 weeks. Stability differences were seen with different EC PUDs and with different pigments, but good results were obtained for some inkjet inks.

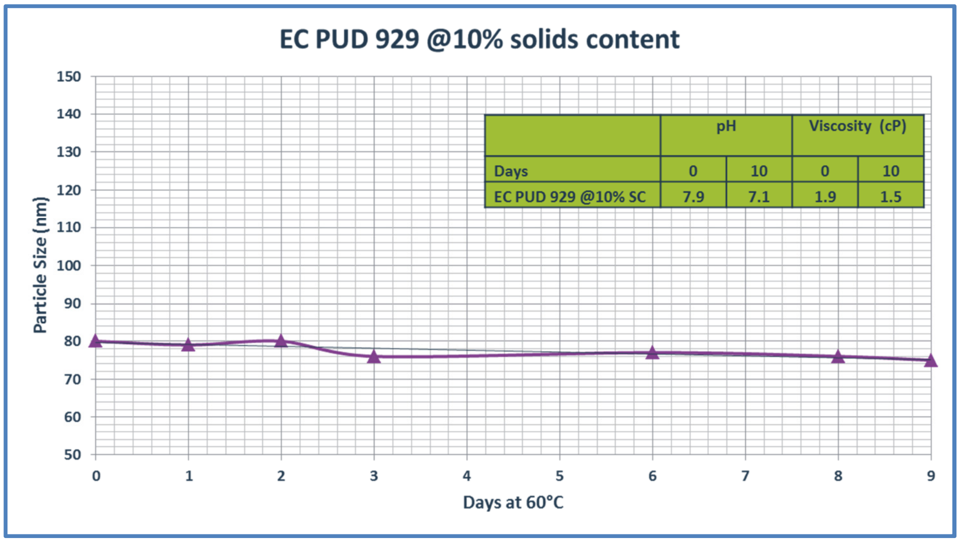
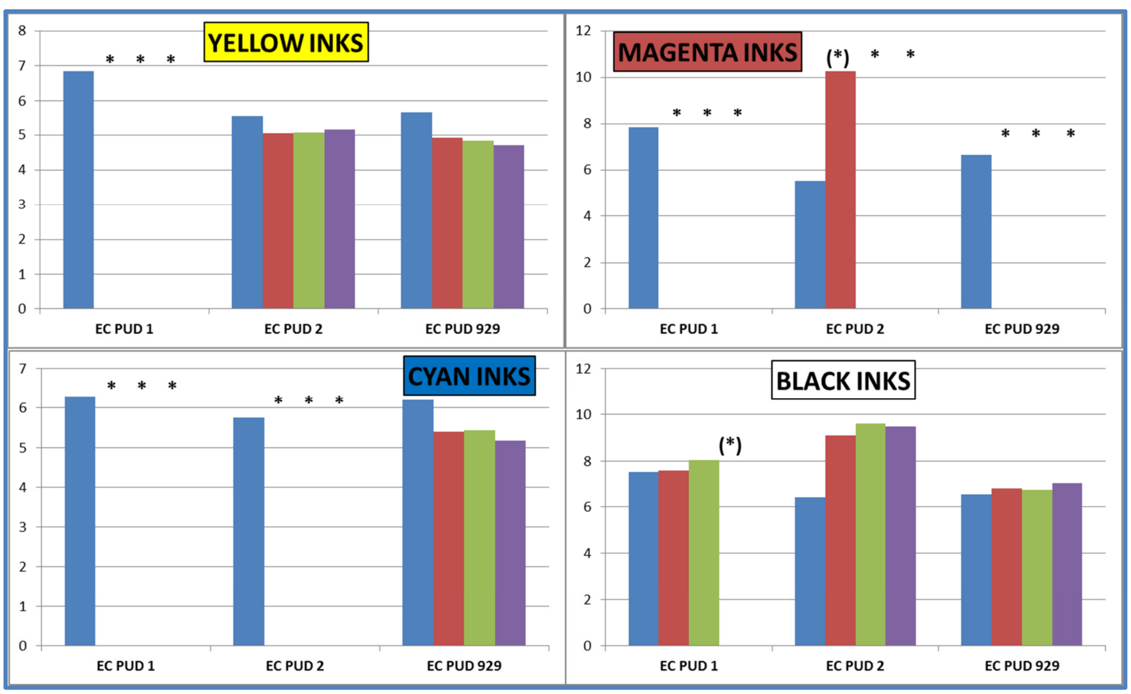


Figure 4. Stability Test Results for EC PUD 929



*** = sedimentation**

Figure 5. Viscosity Evolution (cP) of EC PUD Inkjet Inks at 50° C at 0, 2, 4, and 6 Weeks

INK FILTERABILITY & JETTABILITY

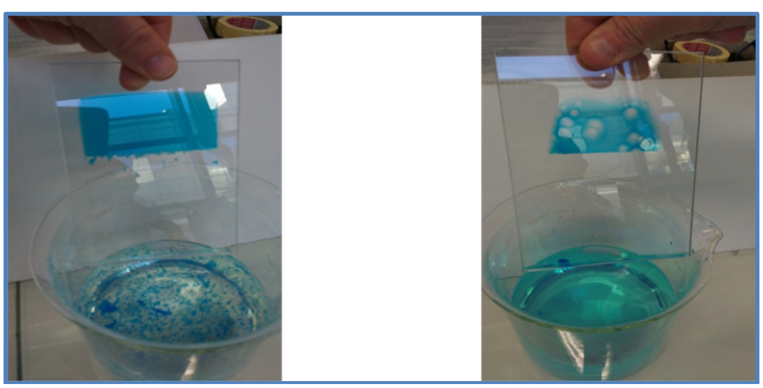
The EC PUDs and the inkjet inks are filtered to remove particles that might damage or clog the nozzles. This must be easily accomplished without too much time and without excessive clogging of the filters. For ease in filtering the EC PUD, there is a specification on the amount of 50+ micron grits, typically < 10 mg/L. The inkjet ink must, obviously, be jettable. Filterability and jettability were tested on inkjet inks using the formulation shown in Table 3. Dimatix disposable piezo print heads were used in the jetting experiments. All CMYK inkjet inks could be filtered and jetted.

Table 3. Waterbased EC PUD Inkjet Ink

Step 1 : Prepare pigment dispersion	
Water	13.85
Pigment wetting agent	2.00
Defoamer	0.10
Biocide	0.05
Pigment	4.00
Step 2 : Add the following letdown to the pigment dispersion	
EC PUD 1	24.00
Water	32.90
Propylene glycol	19.00
Substrate wetting agent	0.10
Surface tension modifier	1.00
Photoinitiator	3.00

INK RESOLUBILITY

Ink resolubility before cure is important to avoid drying in the print heads and blocking the nozzles. As discussed earlier, inkjet inks based on EC PUDs separate the drying step from the curing step, and are resoluble after dry but before cure. Thus, these inks do not block the nozzles. Figure 6 shows the resolubility after drying for several pigmented EC PUDs. (The dried films (on glass) were placed in water at room temperature for 1 minute.) All are resoluble, with EC PUD 929 a little less so.



EC PUD 929 **EC PUD 953, EC PUD 1, EC PUD 2**

Figure 6. Resolubility of EC PUDs

INK REACTIVITY

Ink reactivity, or cure speed, can be impacted by several variables. These include double bond concentration of the ink, photoinitiator concentration, lamp type and output (wavelength and intensity), pigment color and concentration, and ink thickness, to name a few. With UV LED lamps, oxygen inhibition of the free radical polymerization also impacts surface cure speed.

Figure 7 shows the surface cure speed in meters/minute for CMYK inks (proprietary formulations) based on five EC PUDs. (CMYK = Cyan, Magenta, Yellow, Black. The colors of the bar graphs correspond to the ink colors.) The inks were applied on Leneta charts at 15 microns (wet), dried in a 60°C oven for four minutes, and cured using full spectrum mercury lamps (200 watts/cm at 70% power). Surface cure was measured via the graphite test for CMY inks, and by the talc test for black (K) inks. EC PUD 929 had the fastest cure speed for all color inks. The EC PUD 929 has the lowest weight per double bond (172), but EC PUD 3 has the highest (602). So, it does not appear that weight per double bond is a major factor in determining cure speed.

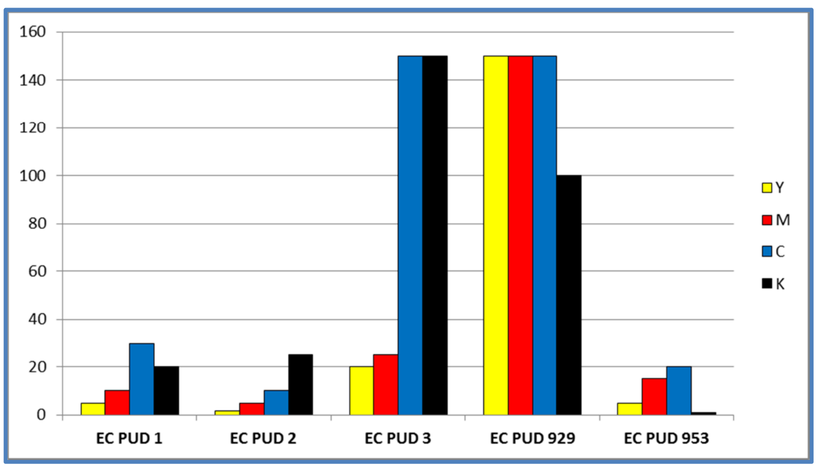


Figure 7. Cure Speed (m/min) of EC PUD Based CMYK Inkjet Inks with Mercury Lamps

UV LED cure speeds were also determined for clear coatings of EC PUDs. A #5 wire wound bar was used to apply the coating to a plastic substrate, which was dried for 10 minutes in a 60°C oven to yield a 5 micron coating. For curing, a 16 watt/cm^2, 395 nm UV LED lamp was used at a cure distance of 1 cm. Surface cure was measured via the graphite test.

The clear coatings were prepared by adding photoinitiator to the EC PUD, and incorporating with a commercial mixer. Either ethyl (2,4,6-trimethylbenzoyl) phenyl phosphinate (TPO-L) or a water dispersion of phosphine oxide, phenyl bis (2,4,6-trimethyl benzoyl) (BAPO) was used at various concentrations.

Since EC PUD 929 was the fastest curing EC PUD with the mercury lamp (>150 m/min), it was chosen for the UV LED cure evaluations. With TPO-L as the photoinitiator at 1.5, 3.0 and 6.0% levels, surface cure speeds of 12 fpm (~5000 mJ/cm^2) were obtained for all PI concentrations. Changing the PI to BAPO at 1.5, 3.0, and 6.6% levels resulted in uncured surfaces of the coatings when cured at 12 fpm. This is surprising, as BAPO has a higher extinction coefficient compared to TPO-L. However, BAPO was more difficult to incorporate versus the TPO-L, and this may have resulted in lower effective BAPO concentrations. (Even though the BAPO was water dispersed, a hazy product resulted after mixing with the EC PUD.) Work continues in this area, to try to improve the surface cure speed of UV LED cured EC PUD based clear coatings.

Figure 8 shows the double bond conversion of the EC PUD 929 based clear coating with different PI levels and different cure temperatures. Conversion was measured by ATR-FTIR at 1.66 microns depth using the peak area at 810 cm^{-1} (C=C), and the reference peak area at 764 cm^{-1}.

Higher double bond conversions were obtained with TPO-L versus BAPO, consistent with the cure speed results. (The exception was the 6% PI level cured at 90°C.) For room temperature cure, 1% TPO-L was as good as 3 or 6%. At 90°C, 3.0% TPO-L gave the best double bond conversion. For BAPO, 6% levels gave the best double bond conversion for both cure temperatures.

Increasing the cure temperature provides better mobility for free radicals in the coating, and extends the time to reach the gel point. Both of these aspects will result in better double bond conversion, as generally shown in Figure 8.

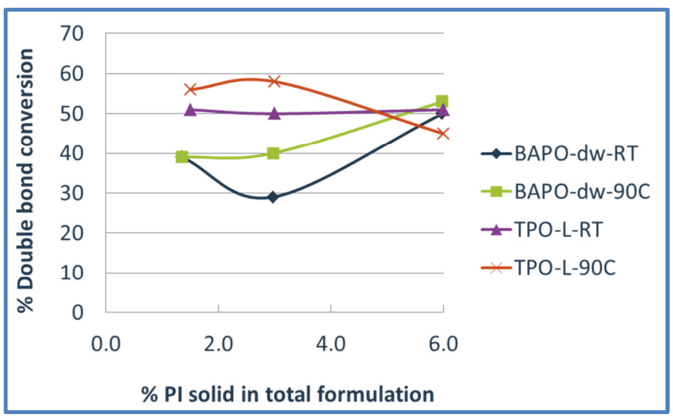


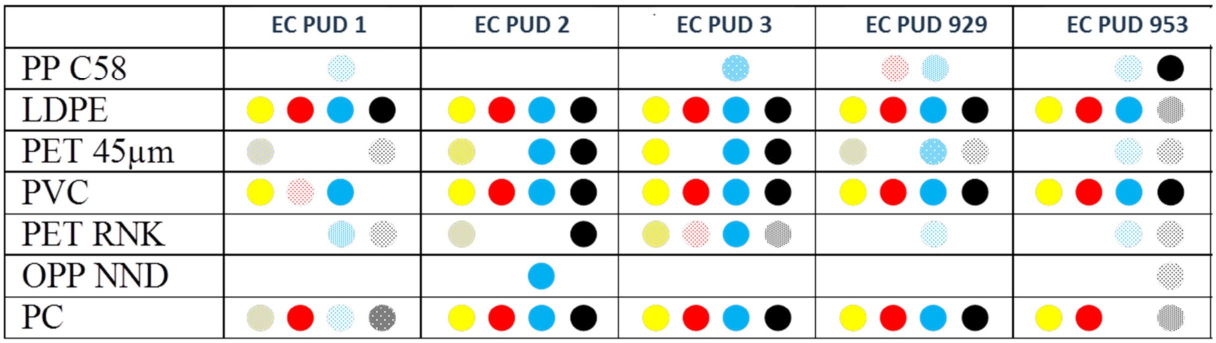
Figure 8. Double Bond Conversion in EC PUD 929 Based Coatings

INK PERFORMANCE PROPERTIES

The cured inkjet ink must have adhesion to the substrate and provide the desired performance for the application. Table 4 shows the adhesion of CMYK inks based on EC PUDs to various substrates. The inks were applied on corona treated filmic substrates at 15 microns (wet), dried in a 60°C oven for four minutes, and cured using full spectrum mercury lamps (200 watts/cm at 70% power). Adhesion was tested by tape pull with TESA 4104 tape. The colors of the dots correspond to the C, M, Y, or K ink, and the intensity of the dot reflects the amount of adhesion (darker dot = better adhesion). It was easier to obtain adhesion to some substrates (LDPE, PVC, PC), and some EC PUDs (2 and 3) provided better adhesion to multiple substrates.

The adhesion of the clear coatings based on various EC PUDs and cured with UV LED is shown in Table 5. The coating (EC PUD and 3% TPO-L) was applied to the untreated filmic substrate with a #5 wire wound bar, and dried for 10 minutes in a 60°C oven to yield a 5 micron coating. Cure was at room temperature at 12 fpm with a 16 watt/cm^2, 395 nm UV LED lamp, at a distance of 1 cm (~ 5000 mJ/cm^2). Adhesion was tested via tape pull (3M 600 and 610 tapes), and reported as percent coating that remained on the substrate.

Table 4. Adhesion of CMYK Inkjet Inks Based on EC PUDs



PP= polypropylene LDPE= low density polyethylene PET= polyethylene terephthalate
PVC= polyvinyl chloride OPP= oriented polypropylene PC= polycarbonate

Table 5. Adhesion of Clear Coatings Based on EC PUDs
(reported as % coating that remains after tape pull)

Substrate	Tape #	EC PUD 912	EC PUD 929	EC PUD 953	EC PUD 1	EC PUD 2	EC PUD 3
PC	600	100	100	30	80	100	50
	610	90	100	100	90	90	100
Rigid PVC	600	100	100	100	100	100	100
	610	100	100	100	100	100	100
White PE	600	0	100	100	20	30	0
	610	95	100	100	100	100	90
HIPS	600	100	100	100	100	100	100
	610	100	100	100	100	100	100
White PP	600	100	100	50	0	0	10
	610	100	100	100	100	50	100
PET	600	100	100	100	0	100	80
	610	80	100	90	90	90	100
Average Adhesion		**88.8**	**100**	**89.2**	**73.3**	**80**	**77.5**

PC= polycarbonate PVC= polyvinyl chloride PE= polyethylene
HIPS= high impact polystyrene PP= polypropylene PET= polyethylene terephthalate

With rigid PVC and HIPs, 100% adhesion was obtained for all EC PUD coatings. The coating based on EC PUD 929 had 100% adhesion to all of the substrates. EC PUD 912 and EC PUD 953 were also good for adhesion, with an average adhesion of just less than 90%. All EC PUDs achieved 100% adhesion to some substrates.

Generally, adhesion is related to through cure. These adhesion data show that through cure was achieved for all EC PUDs, even though surface cure was not. (Under these cure conditions, only EC PUD 929 achieved surface cure via the graphite test.) Cure with UV LED lamps generally provides better through cure than surface cure because of their longer wavelength emissions. These longer wavelengths are preferentially absorbed in the coating depth, and not at the surface, resulting in better depth of cure.

CONCLUSIONS

Waterbased EC inkjet inks are an alternative to both waterborne inkjet inks and 100% solids EC inkjet inks, and bring multiple benefits over the other technologies. EC PUDs can be designed to provide low migration and low extractables, and this provides the potential to formulate waterbased EC inkjet inks and coatings for food packaging.

Inkjet inks based on EC PUDs have been shown to be thermally stable, filterable, and jettable. These inks are also resoluble after dry but before cure, insuring that nozzle blockage does not occur. Reactivity of waterbased inkjet inks cured with full spectrum mercury lamps is dependent on the choice of the EC PUD, but can be quite fast. These inkjet inks also have good adhesion to many corona treated filmic substrates. UV LED surface cure speed of EC PUD clear coatings needs improvement, but through cure is quite good, providing excellent adhesion to multiple untreated filmic substrates.

ACKOWLEDGEMENTS

My co-authors for all of the experimental results that were presented in this paper.

ADDENDUM

SURFACE CURE TEST METHODS

Graphite and Talc Tests: These are surface cure tests. The graphite or talc is sprinkled on the surface of the cured ink or coating, and then gently brushed off with a cotton ball. The amount of graphite or talc that remains is visually assessed. The visual assessment is made easier by using the graphite test on clear coatings, and CMY inks, and the talc on black inks.