Ebeam Inkjet Technology for Low Migration Digital Printing Applications

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ABSTRACT

Electron beam (EB) curing enables a wide window for formulating inks for food packaging and other low migration applications. Since these inks do not require photoinitiators, two major concerns associated with them namely, odor and migration, are eliminated. Inkjet printing offers unique features such as variable data printing & late-stage customization. In this study, we have characterized the EB curing of inkjet inks in a mono-color, single-pass configuration on food packaging substrates. Discussion of process variables and recommendations are included.

INTRODUCTION

EB technology offers enormous benefits, including an extremely precise and consistent energy output that does not drift over time. In addition, EB technology is also capable of yielding instantaneous cure at very fast line production speeds. Furthermore, EB units generate minimal heat and consume 95% less energy than thermal drying, and up to 80% less energy than standard UV curing.

Recent developments in EB curing units have also reduced their footprint, effectively making them easier to install on new and existing production lines. In addition, the cost of EB units has also decreased in recent years, making EB a competitive alternative from a cost standpoint as well[1]. The combination of these features makes EB an option for curing inks to be used in food packaging and other low migration applications.

EXPERIMENTAL

Inks

Three EB Black inkjet inks comprising combinations of three acrylate monomers were formulated for this study. These specific acrylate monomers were selected because they each comply with currently accepted food packaging guidelines.

Monomer 1: Acrylic Acid Ester
Monomer 2: Alkoxylated Acrylic Monomer

Monomer 3: Low-Extractables Alkoxylated Acrylic Monomer

Ink 1: Monomers 1 and 2
Ink 2: Monomers 1, 2, and 3
Ink 3: Monomers 2 and 3

Carbon Black pigment was dispersed within the monomers to obtain opacity comparable to UV/LED Curable Black inks that are used for standard food packaging and low migration applications.

Substrates

These were printed on commercial food packaging stock EFS-032 (Substrate #1) and EFO-225 (Substrate #2) supplied from Glenroy, Inc. FTIR samples were generated on a clear PET Film supplied from Mitsubishi Polyesters.

Printing and Curing Conditions

The inks were printed using a Fujifilm Dimatix SG-1024 M-A print head with 30pL drop size. The inks were cured with a 300MRad-m/min EB curing unit, made by PCT. The inks were cured at an oxygen level of 100ppm, with EB doses ranging from 1MR to 5MR in intervals of 1 MR.

To observe the impact of percent ink coverage in terms of film thickness, samples of the optimal ink formula (Ink #3) were also generated at 400dpi x 400dpi in addition to the initial 400dpi x 200dpi samples. In terms of film thickness, the print resolution of 400dpi x 200dpi yielded a theoretical film weight of 2.40 $\mu L/in^2$. For comparison, the print resolution of 400dpi x 400dpi yielded a theoretical film weight of 4.80 $\mu L/in^2$.

Tape Test Adhesion

Tape test adhesion using 3M 600 tape was the initial test conducted to verify adhesion of the EB cured inks to the substrates.

Dry and Solvent Rub Resistance

Dry rub resistance provides an indication of an ink's ability to maintain adhesion during handling, filling, and packaging operations within a production environment. MEK (Methyl Ethyl Ketone) rub resistance is used to determine the ink resistance to final packaging, product and cleaning operations. All rub resistance testing was completed using an RT-300 Rub Resistance Tester, which is manufactured by Daiea Kagaku Seiki Mfg. Co. Ltd.

Specifically, for dry rub resistance, a dry white cotton reference cloth was clamped onto a calibrated metal weight. The printed and cured samples were then subjected to 100 rubs over a

100mm distance with each rub repetition. In regards to MEK rub resistance, the white cotton reference cloth was first soaked with 100uL of MEK. The printed and cured MEK Samples were then immediately subjected to 5 rubs over a 100mm distance with each rub repetition.

The resulting color change (ΔE) was measured on the reference cloth using a spectrophotometer. The results were then reported on a Gray Scale Value of (1, 1-2, 2, 2-3, 3, 3-4, 4, 4-5, and 5). In regards to the Gray Scale Values, please see Table 1 below which correlates the measured Color Change (ΔE) to the corresponding Gray Scale Value (GSc).

Gray Scale Value Chart:		
Color Change ΔE:		**GSc:**
	< 0.40	**5**
≥ 0.40	< 1.25	**4-5**
≥ 1.25	< 2.10	**4**
≥ 2.10	< 2.95	**3-4**
≥ 2.95	< 4.10	**3**
≥ 4.10	< 5.80	**2-3**
≥ 5.80	< 8.20	**2**
≥ 8.20	< 11.60	**1-2**
≥ 11.60		**1**

Table 1. Gray Scale Value Chart. This table correlates the measured Color Change (ΔE) to corresponding Gray Scale Values (GSc). There are 9 potential Gray Scale Values ranging from (1, 1-2, 2, 2-3, 3, 3-4, 4, 4-5, and 5). These Gray Scale Values were used when conducting Dry and Solvent Rub Resistance Tests.

FTIR Analysis of Acrylate Conversion

Since food packaging and other low migration applications have specific limits on migration, it is critical that unreacted acrylates be minimized. The conversion of acrylates present within the EB inks were therefore measured through FTIR analysis. The printed side of the Clear PET film was clamped into the Reflectance cell (ATR) of a Shimadzu FTIR 8400S spectrophotometer. The analysis was carried out using a 2.0 cm^{-1} resolution with 20 scans at 2.8mm/second. The particular analyte of interest was the acrylate vinyl group, which has a characteristic peak at 810/cm.

RESULTS

Tape Test Adhesion: 600 Tape			**Pass/Fail:**				
Ink:	**Substrate:**	**DPI:**	**1MR:**	**2MR:**	**3MR:**	**4MR:**	**5MR:**
#1	#1	400 x 200	Pass	Pass	Pass	Pass	Pass
#2	#1	400 x 200	Pass	Pass	Pass	Pass	Pass

#3	#1	400 x 200	Pass	Pass	Pass	Pass	Pass
#3	#1	400 x 400	Pass	Pass	Pass	Pass	Pass

Table 2. Tape Test Adhesion on Substrate #1: 600 Tape. This table demonstrates the Pass/Fail results obtained while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. For this data set, the three inks were printed on Substrate #1 at 400dpi x 200dpi resolution. In addition, Ink #3 was also printed on Substrate #1 at 400dpi x 400dpi resolution. Tape Test Adhesion was completed using 3M 600 Tape after EB cure at each respective dose. Each data point represents an average of n=3 trial replicates.

Tape Test Adhesion: 600 Tape			**Pass/Fail:**				
Ink:	**Substrate:**	**DPI:**	**1MR:**	**2MR:**	**3MR:**	**4MR:**	**5MR:**
#1	#2	400 x 200	Pass	Pass	Pass	Pass	Pass
#2	#2	400 x 200	Pass	Pass	Pass	Pass	Pass
#3	#2	400 x 200	Pass	Pass	Pass	Pass	Pass
#3	#2	400 x 400	Pass	Pass	Pass	Pass	Pass

Table 3. Tape Test Adhesion on Substrate #2: 600 Tape. This table demonstrates the Pass/Fail results obtained while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. For this data set, the three inks were printed on Substrate #2 at 400dpi x 200dpi resolution. In addition, Ink #3 was also printed on Substrate #2 at 400dpi x 400dpi resolution. Tape Test Adhesion was completed using 3M 600 Tape after EB cure at each respective dose. Each data point represents an average of n=3 trial replicates.

Dry Rub Resistance			**Color Change ΔE:**				
Ink:	**Substrate:**	**DPI:**	**1MR:**	**2MR:**	**3MR:**	**4MR:**	**5MR:**
#1	#1	400 x 200	22.54	0.36	0.28	0.17	0.13
#2	#1	400 x 200	0.52	0.13	0.13	0.14	0.10
#3	#1	400 x 200	0.24	0.21	0.18	0.16	0.14
#3	#1	400 x 400	0.30	0.29	0.22	0.16	0.12

Table 4. Dry Rub Resistance on Substrate #1: Color Change (ΔE) vs. Dose. This table demonstrates the Color Change (ΔE) obtained while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. For this data set, the three inks were printed on Substrate #1 at 400dpi x 200dpi resolution. In addition, Ink #3 was also printed on Substrate #1 at 400dpi x 400dpi resolution. Dry Rub Resistance testing was completed with 100 Rubs over a 100mm distance. Each data point represents an average of n=3 trial replicates.

Dry Rub Resistance			**Color Change ΔE:**				
Ink:	**Substrate:**	**DPI:**	**1MR:**	**2MR:**	**3MR:**	**4MR:**	**5MR:**
#1	#2	400 x 200	6.70	0.28	0.19	0.15	0.12
#2	#2	400 x 200	0.31	0.26	0.17	0.15	0.10
#3	#2	400 x 200	0.32	0.24	0.19	0.14	0.10

#3	#2	400 x 400	0.38	0.30	0.23	0.16	0.14

Table 5. Dry Rub Resistance on Substrate #2: Color Change (ΔE) vs. Dose. This table demonstrates the Color Change (ΔE) obtained while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. For this data set, the three inks were printed on Substrate #2 at 400dpi x 200dpi resolution. In addition, Ink #3 was also printed on Substrate #2 at 400dpi x 400dpi resolution. Dry Rub Resistance testing was completed with 100 Rubs over a 100mm distance. Each data point represents an average of n=3 trial replicates.

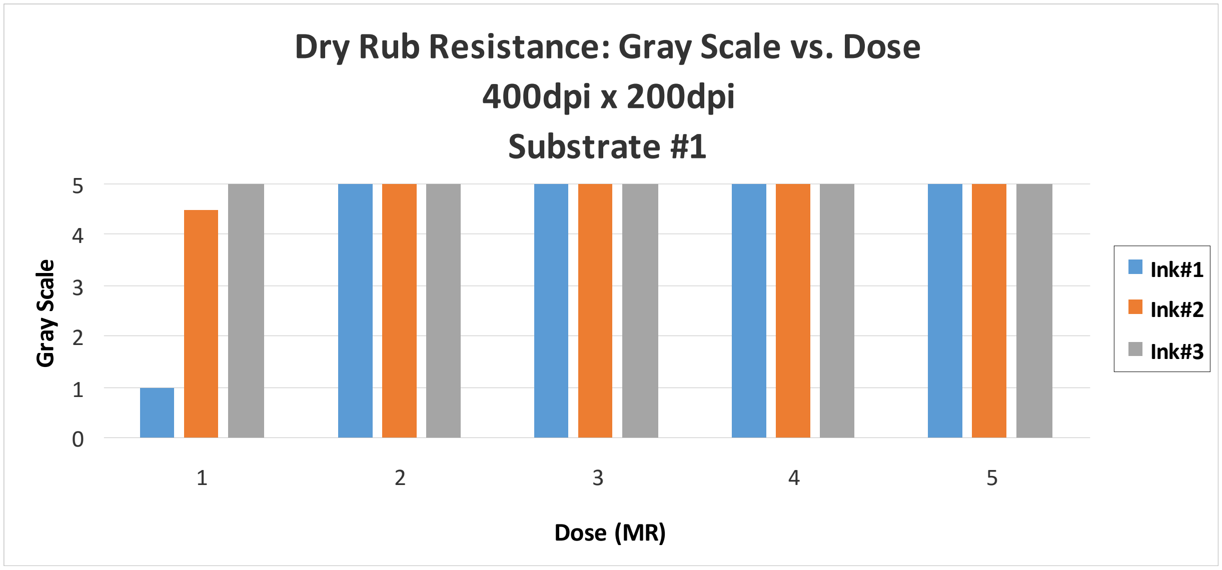


Figure 1. Dry Rub Resistance on Substrate #1: Gray Scale vs. Dose. This graph demonstrates the Gray Scale values obtained while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. For this data set, the three inks were printed on Substrate #1 at 400dpi x 200dpi resolution. Dry Rub Resistance testing was completed with 100 Rubs over a 100mm distance. Each data point represents an average of n=3 trial replicates.

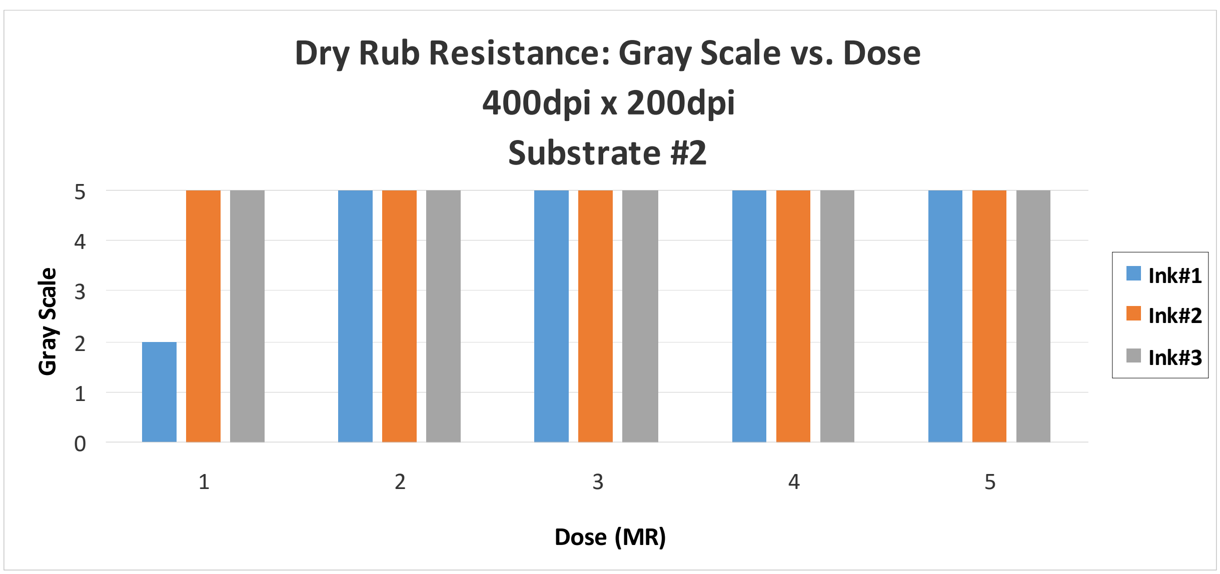


Figure 2. Dry Rub Resistance on Substrate #2: Gray Scale vs. Dose. This graph demonstrates the Gray Scale values obtained while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. For this data set, the three inks were

printed on Substrate #2 at 400dpi x 200dpi resolution. Dry Rub Resistance testing was completed with 100 Rubs over a 100mm distance. Each data point represents an average of n=3 trial replicates.

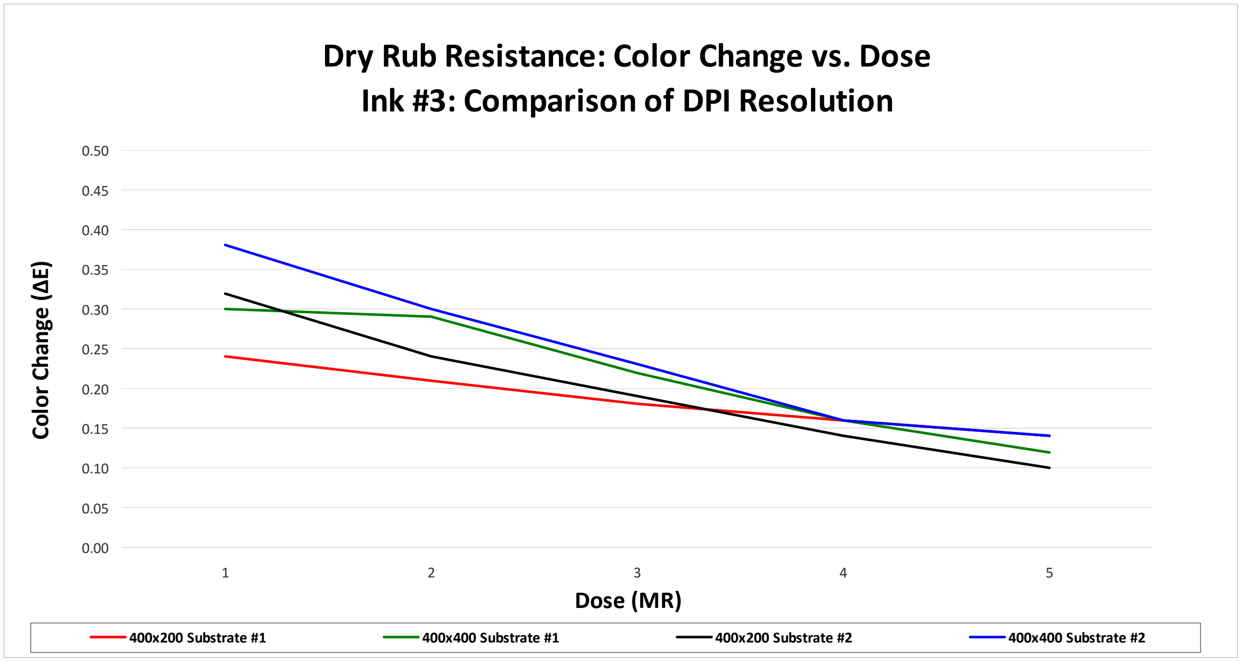


Figure 3. Dry Rub Resistance for Ink #3: Gray Scale vs. Dose. This graph demonstrates the Gray Scale values obtained while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. For this data set, Ink #3 was printed on Substrate #1 and Substrate #2, at 400dpi x 200dpi and 400dpi x 400dpi. Dry Rub Resistance testing was completed with 100 Rubs over a 100mm distance. Each data point represents an average of n=3 trial replicates.

MEK Rub Resistance			Color Change ΔE:				
Ink:	Substrate:	DPI:	1MR:	2MR:	3MR:	4MR:	5MR:
#1	#1	400 x 200	50.99	24.86	0.90	0.50	0.35
#2	#1	400 x 200	38.09	0.82	0.33	0.22	0.17
#3	#1	400 x 200	0.87	0.27	0.23	0.19	0.34
#3	#1	400 x 400	0.54	0.28	0.15	0.13	0.17

Table 6. MEK Rub Resistance on Substrate #1: Color Change (ΔE) vs. Dose. This table demonstrates the Color Change (ΔE) obtained while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. For this data set, the three inks were printed on Substrate #1 at 400dpi x 200dpi resolution. In addition, Ink #3 was also printed on Substrate #1 at 400dpi x 400dpi resolution. MEK Rub Resistance testing used an injection volume of 100uL MEK, and completed 5 MEK Rubs over a 100mm distance. Each data point represents an average of n=3 trial replicates.

MEK Rub Resistance			Color Change ΔE:				
Ink:	Substrate:	DPI:	1MR:	2MR:	3MR:	4MR:	5MR:
#1	#2	400 x 200	51.04	23.59	2.52	1.47	0.93
#2	#2	400 x 200	46.32	2.08	1.14	0.64	0.65

#3	#2	400 x 200	1.37	0.24	0.35	0.16	0.23
#3	#2	400 x 400	0.31	0.34	0.23	0.20	0.14

Table 7. MEK Rub Resistance on Substrate #2: Color Change (ΔE) vs. Dose. This table demonstrates the Color Change (ΔE) obtained while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. For this data set, the three inks were printed on Substrate #2 at 400dpi x 200dpi resolution. In addition, Ink #3 was also printed on Substrate #2 at 400dpi x 400dpi resolution. MEK Rub Resistance testing used an injection volume of 100uL MEK, and completed 5 MEK Rubs over a 100mm distance. Each data point represents an average of n=3 trial replicates.

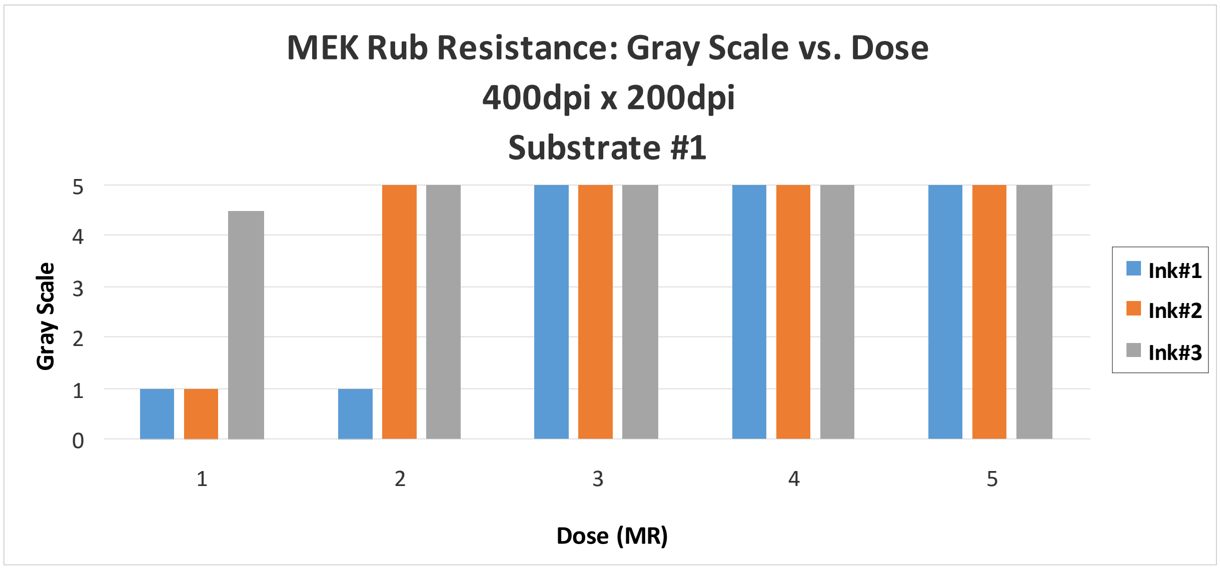


Figure 4. MEK Rub Resistance Substrate #1: Gray Scale vs. Dose. This graph demonstrates the Gray Scale values obtained while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. For this data set, the three inks were printed on Substrate #1 at 400dpi x 200dpi resolution. MEK Rub Resistance testing used an injection volume of 100uL MEK, and completed 5 MEK Rubs over a 100mm distance. Each data point represents an average of n=3 trial replicates.

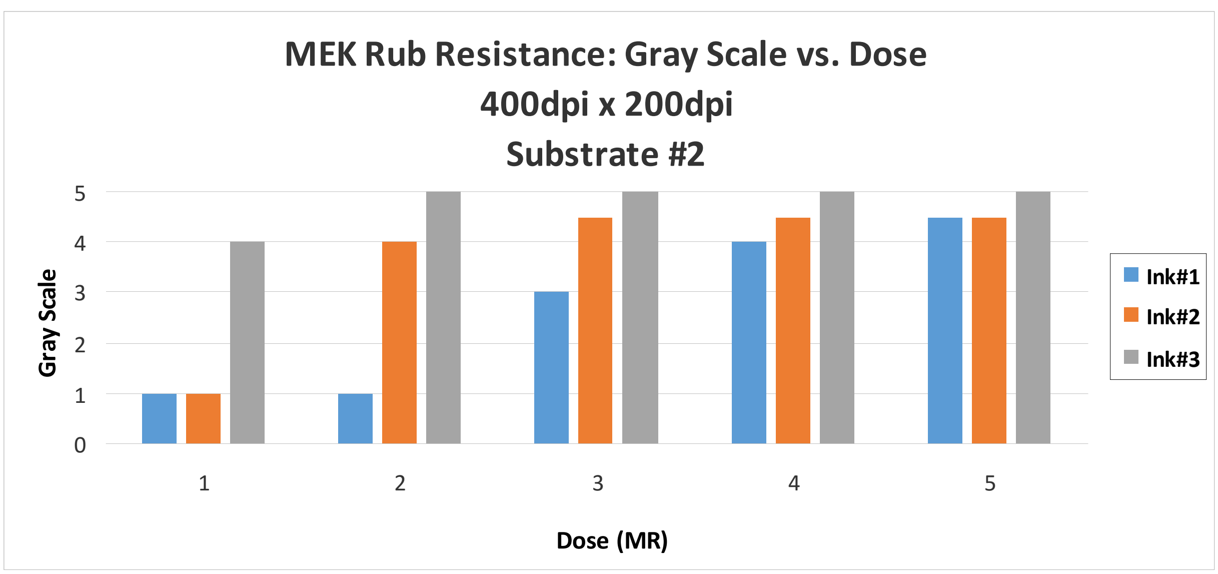


Figure 5. MEK Rub Resistance Substrate #2: Gray Scale vs. Dose. This graph demonstrates the Gray Scale values obtained while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. For this data set, the three inks were printed on Substrate #2 at 400dpi x 200dpi resolution. MEK Rub Resistance testing used an injection volume of 100uL MEK, and completed 5 MEK Rubs over a 100mm distance. Each data point represents an average of n=3 trial replicates.

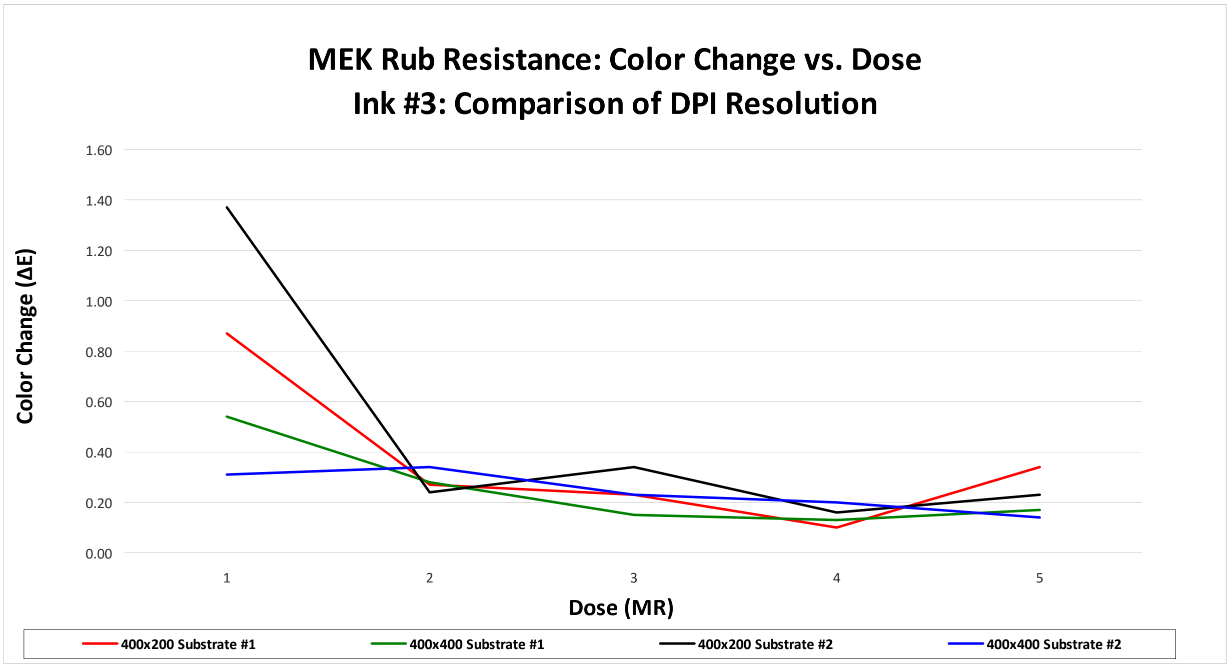


Figure 6. MEK Rub Resistance for Ink #3: Gray Scale vs. Dose. This graph demonstrates the Gray Scale values obtained while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. For this data set, Ink #3 was printed on Substrate #1 and Substrate #2, at 400dpi x 200dpi and 400dpi x 400dpi. MEK Rub Resistance testing used an injection volume of 100uL MEK, and completed 5 MEK Rubs over a 100mm distance. Each data point represents an average of n=3 trial replicates.

FTIR Analysis of Acrylate Conversion

The acrylate vinyl group has a characteristic peak at 810/cm due to out-of-plane bending. The FTIR scans of the three inks show this peak within the uncured inks, and its disappearance after curing at various dose levels between 1MR to 5 MR. All of the EB cured inks were printed on a clear PET film for FTIR analysis. For reference, please see the attached FTIR Scans located in the Appendix. Ink #1 at 400dpi x 200dpi resolution corresponds with Figure 7, Ink #2 at 400dpi x 200dpi resolution corresponds with Figure 8, Ink #3 at 400dpi x 200dpi resolution corresponds with Figure 9, and Ink #3 at 400dpi x 400dpi resolution corresponds with Figure 10.

DISCUSSION

The purpose of this study was to evaluate suitability of EB inkjet technology for low migration digital printing applications. A series of three EB black inkjet inks were cured with EB radiation within a range of 1MR to 5MR on food-grade suitable packaging. Each of the three inks was printed with a Fujifilm Dimatix SG-1024 M-A print head at 400dpi x 200dpi. In addition, Ink #3 was printed at 400dpi x 400dpi to demonstrate the ability of the EBeam to provide full cure even through thick ink films. All conditions were then subjected to a variety of adhesion and cure tests including tape test, dry rub resistance, MEK rub resistance, and FTIR analysis.

As demonstrated within Tables 2 and 3, the cured ink samples passed tape test adhesion with 3M 600 tape in all cases. Despite the increased film thickness at 400dpi x 400dpi and the low EB dose of 1MR, Ink #3 had sufficient cure to achieve the necessary adhesion to pass the test.

Color change (ΔE) and Gray Scale Values resulting from Dry Rub resistance tests provide a way to characterize each ink's adhesion and ability to withstand day-to-day handling, packaging, and cleaning procedures. Table 4 and Table 5 display the recorded color change (ΔE) on Substrates #1 and #2, respectively. Each ink formulation exhibited excellent Dry Rub Resistance from 2MR to 5MR, independent of substrate. It was only at a dose of 1MR that any significant separation in the ability of the inks or substrates is identifiable. Ink #1 resulted in a considerably higher color change, failing on both substrates with corresponding Gray Scale Values of 1 and 2. Figure 1 and Figure 2 reflect the Gray Scale values for all Dry Rub Resistance conditions. In addition, Figure 6 displays the effect of film thickness on rub resistance by demonstrating a comparison of Ink #3 printed at 400dpi x 200dpi vs. 400dpi x 400dpi. Based on the data obtained for Ink #3, EB inkjet technology demonstrates the ability to provide sufficient Dry Rub Resistance at low curing doses, even with increased film thickness.

Similar to Dry Rub Resistance, MEK Rub Resistance tests the ability of an ink to withstand a variety of potential conditions it may be subjected to during the packaging process. Again, the resulting color change (ΔE) and Gray Scale Values provide an effective way to evaluate the suitability of each ink at every condition. Table 6 and Table 7 display the recorded color change (ΔE) on Substrates #1 and #2, respectively. Each Ink formulation had a greater impact on adhesion at lower doses, as shown by the results obtained at 1MR and 2MR. Ink #1 resulted in failure at 1MR and 2MR with a Gray Scale value of 1 in each case. Ink #2 performed slightly better, only resulting in failure at 1MR. Figure 4 and Figure 5 display the Gray Scale values for all MEK Rub Resistance conditions. In addition, these results indicate that each ink was able to achieve better rub resistance on Substrate #1 when compared to Substrate #2. However, independent of substrate, Ink #3 was able to provide sufficient rub resistance at doses of 2MR and above even at 400dpi x 400dpi, as demonstrated within Figure 6.

FTIR scans were used as a method to characterize the extent of cure. The disappearance of the acrylate vinyl group at 810/cm in Figures 7-11 in the Appendix indicate very high conversion of acrylates which minimizes monomer migration and odor.

As demonstrated within this study, with appropriate formulation, EB curing inkjet inks can be extremely effective for food packaging and potentially for other low migration applications. The curing effectiveness that was achieved at low EB doses in turn opens the possibility for higher production speeds as well. In order to expand upon the findings of this current study, migration analysis testing will be conducted via GC-MS through an independent laboratory. Specifically, Ink #3 printed on Substrate #1, will be subjected to testing under FDA conditions of use (E) and

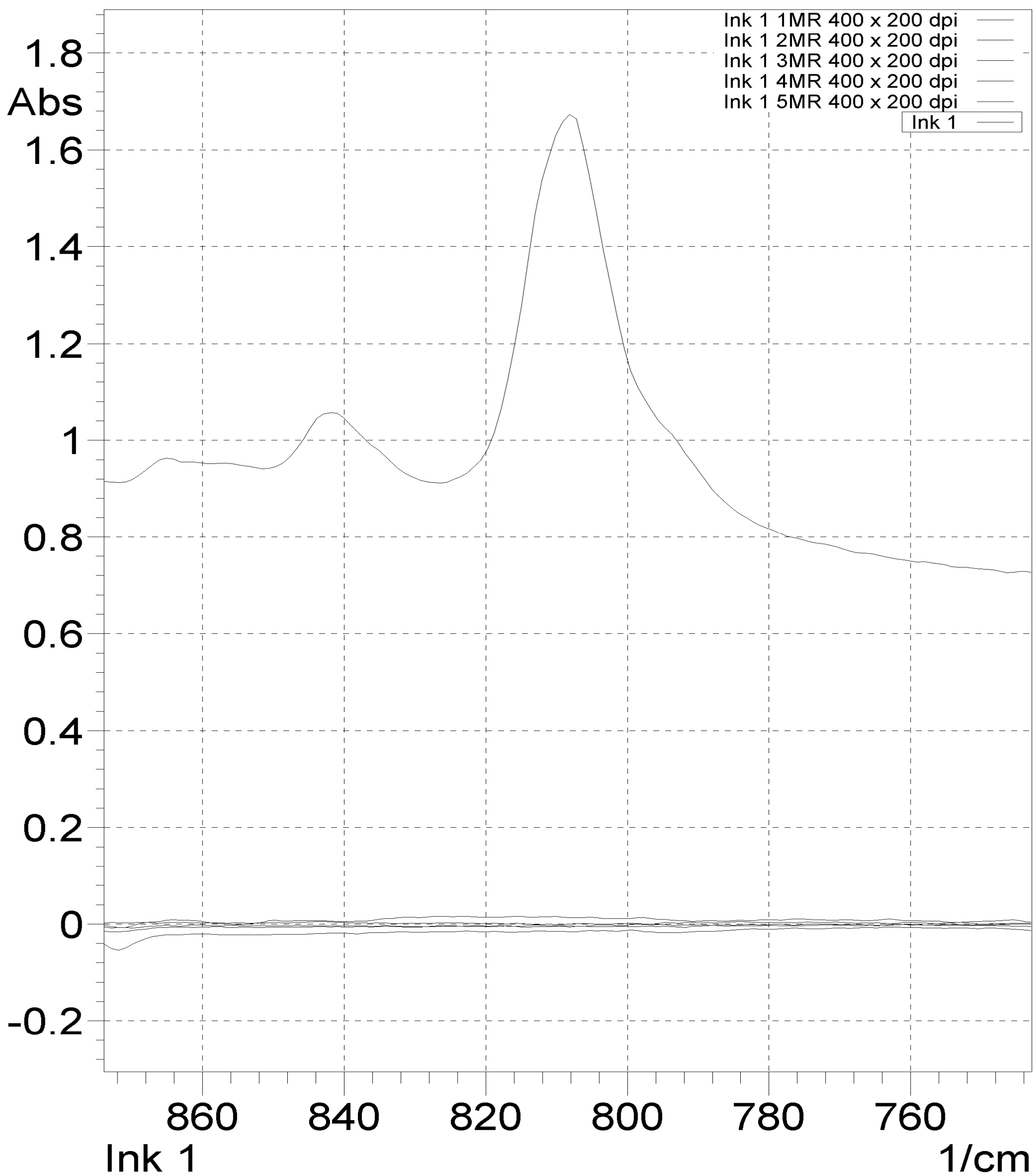
(F).[2] The two curing conditions that will be tested are 1MR and 5MR, both at 400dpi x 200dpi. To conclude, it is our expectation that the migration analysis testing will add further support to the data that we have generated within this study.

REFERENCES

1.http://printplanet.com/forum/what-you-think/editorial/248243-electron-beam-inks-a-versatile-alternative-to-uv

2.http://www.fda.gov/Food/IngredientsPackagingLabeling/PackagingFCS/FoodTypesConditionsofUse/default.htm

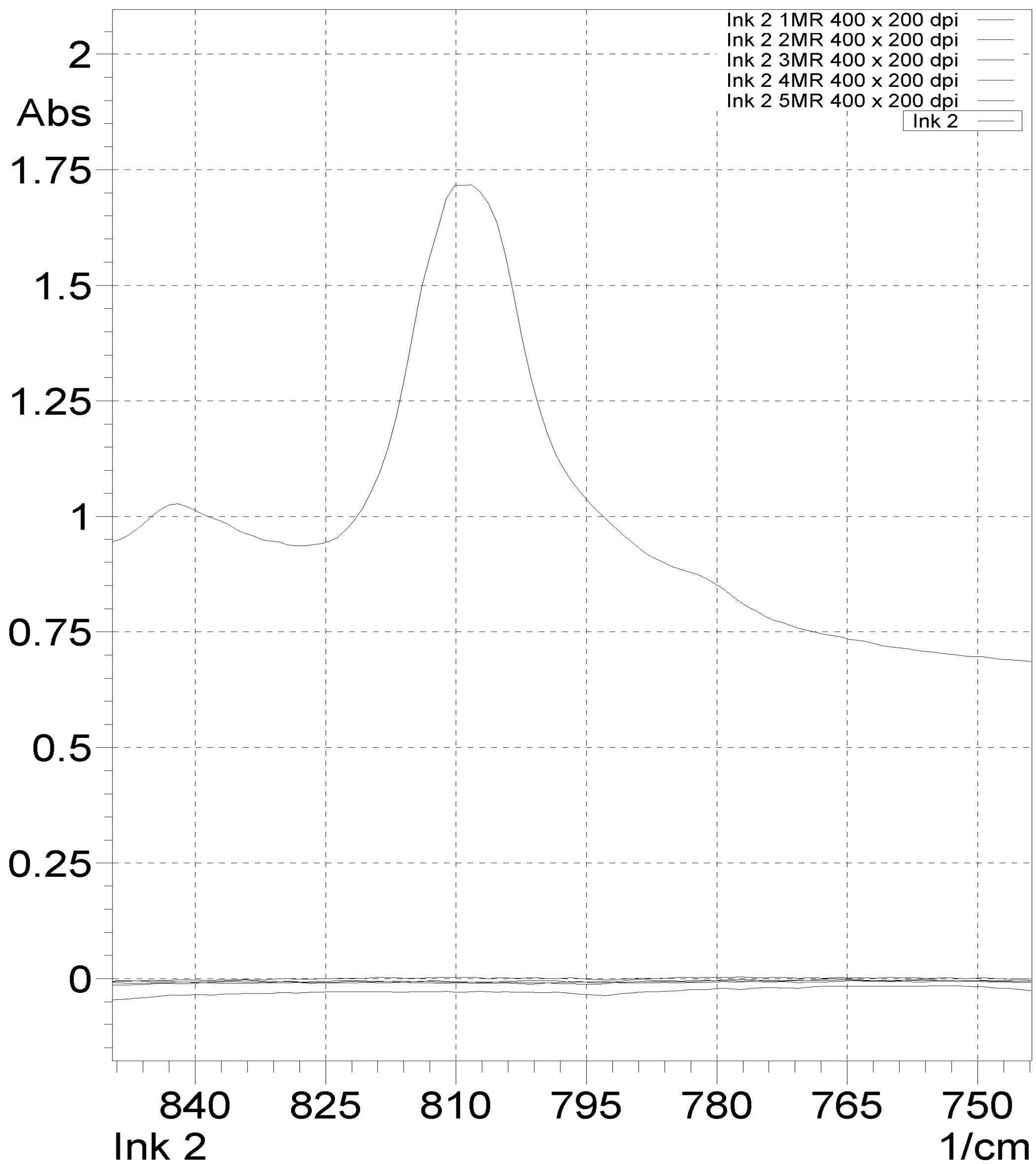
APPENDIX



Comment;
Ink 1 1MR 400 x 200 dpi
Ink 1 2MR 400 x 200 dpi
Ink 1 3MR 400 x 200 dpi
Ink 1 4MR 400 x 200 dpi
Ink 1 5MR 400 x 200 dpi

Date/Time; 02/18/16 08:15:09
No. of Scans; 20
20
20
20
02/18/16 10:59:59

Figure 7. FTIR Scan Ink #1: Absorbance vs. 1/cm. This graph demonstrates For this data set, Ink #1 was first analyzed in liquid form, yielding a characteristic peak at 810/cm. Ink #1 was then printed on a clear PET Film at 400dpi x 200dpi resolution while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. As shown within the FTIR scan, the acrylate vinyl group (810/cm) is minimized upon EB curing, indicating completion of the curing reaction.



Comment;
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Ink 2 2MR 400 x 200 dpi
Ink 2 3MR 400 x 200 dpi
Ink 2 4MR 400 x 200 dpi
Ink 2 5MR 400 x 200 dpi

Date/Time; 02/18/16 10:05:03
No. of Scans; 20
20
20
20
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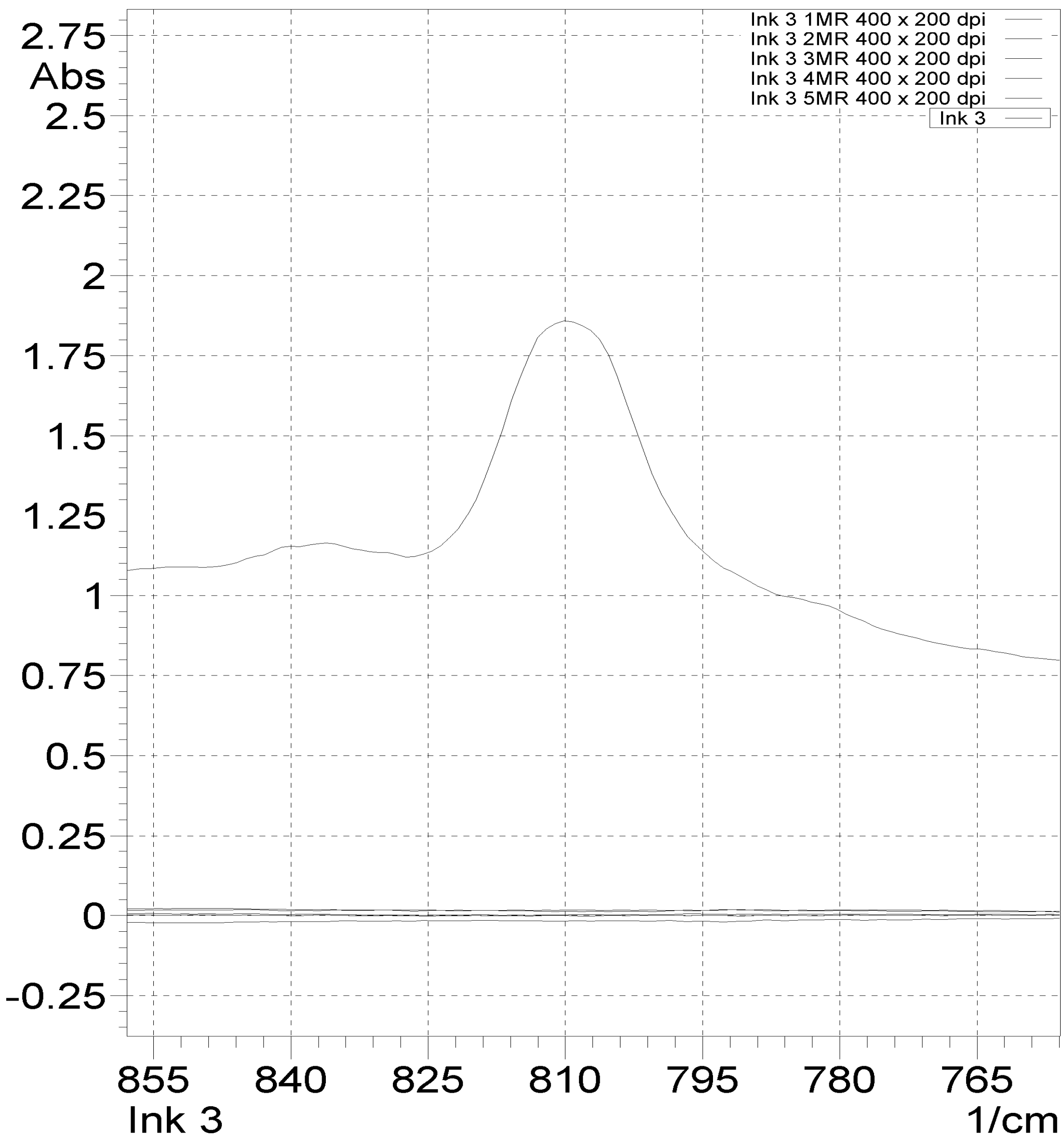
Figure 8. FTIR Scan Ink #2: Absorbance vs. 1/cm. This graph demonstrates For this data set, Ink #2 was first analyzed in liquid form, yielding a characteristic peak at 810/cm. Ink #2 was then printed on a clear PET Film at 400dpi x 200dpi resolution while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. As shown within the FTIR scan, the acrylate vinyl group (810/cm) is minimized upon EB curing, indicating completion of the curing reaction.



Comment;	Date/Time; 02/18/16 09:25:46
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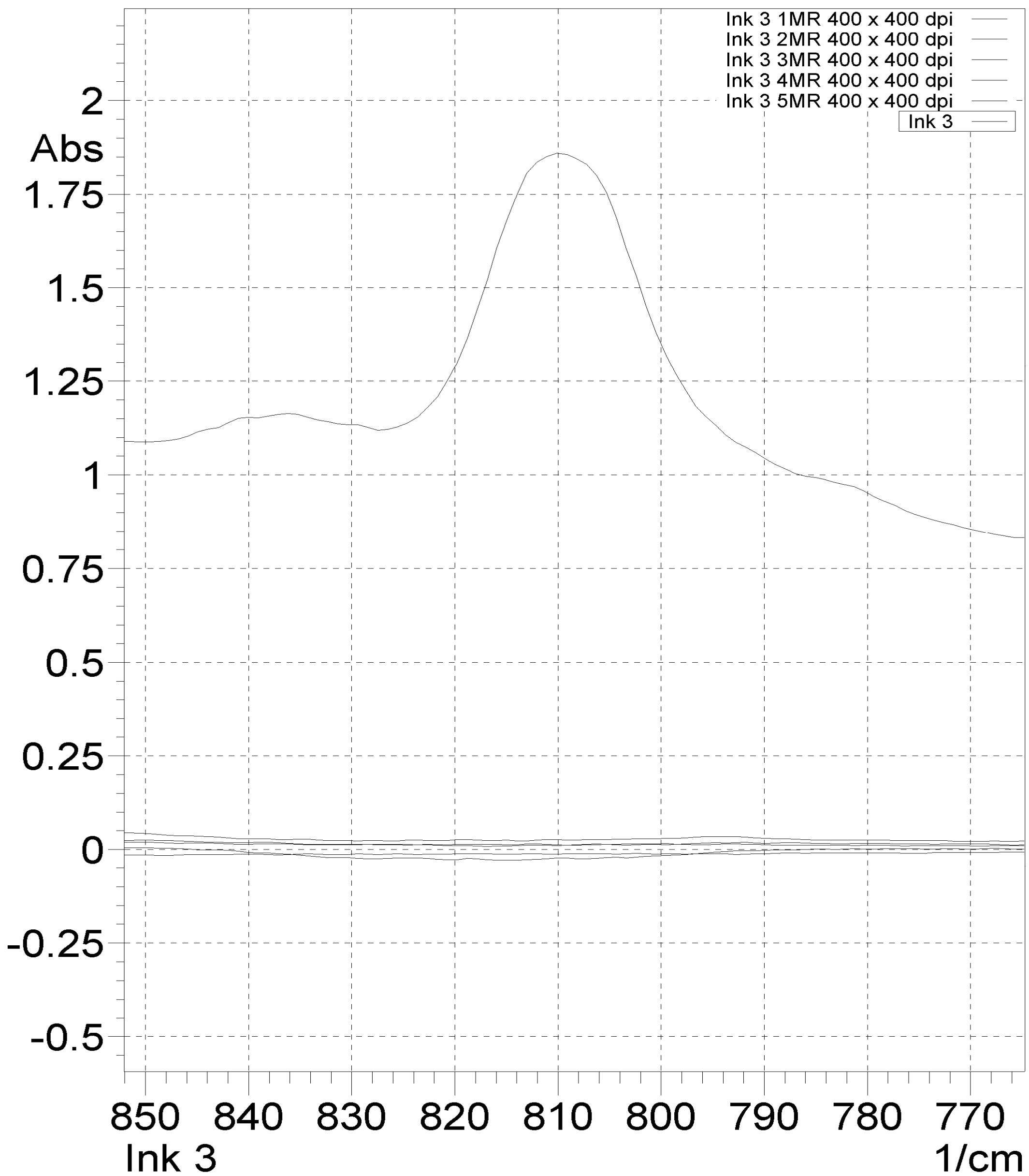
Ink 3 2MR 400 x 200 dpi	20
Ink 3 3MR 400 x 200 dpi	20
Ink 3 4MR 400 x 200 dpi	20
Ink 3 5MR 400 x 200 dpi	02/18/16 11:08:02

Figure 9. FTIR Scan Ink #3: Absorbance vs. 1/cm. This graph demonstrates For this data set, Ink #3 was first analyzed in liquid form, yielding a characteristic peak at 810/cm. Ink #3 was then printed on a clear PET Film at 400dpi x 200dpi resolution while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. As shown within the FTIR scan, the acrylate vinyl group (810/cm) is minimized upon EB curing, indicating completion of the curing reaction.



Comment;
Ink 3 1MR 400 x 400 dpi
Ink 3 2MR 400 x 400 dpi
Ink 3 3MR 400 x 400 dpi
Ink 3 4MR 400 x 400 dpi
Ink 3 5MR 400 x 400 dpi

Date/Time; 02/18/16 09:27:38
No. of Scans; 20
20
20
20
02/18/16 11:08:02

Figure 10. FTIR Scan Ink #3: Absorbance vs. 1/cm. This graph demonstrates For this data set, Ink #3 was first analyzed in liquid form, yielding a characteristic peak at 810/cm. Ink #3 was then printed on a clear PET Film at 400dpi x 400dpi resolution while varying the EB Dose from 1MR to 5MR, in intervals of 1MR. As shown within the FTIR scan, the acrylate vinyl group (810/cm) is minimized upon EB curing, indicating completion of the curing reaction.