# Rapid FTIR Press-Side Testing to Confirm the Cure of UV/EB Coatings for Packaging Applications

Elizabeth Leeper

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**Abstract**

UV and EB curable coatings provide very desirable appearance and resistance properties for surface printed packaging. Coatings suitable for indirect food packaging applications are available; however, they must be properly cured in order to achieve the desired low migration properties. Migration testing using food simulants requires testing by an outside lab and takes at least several days to get results. Testing using reflective (ATR) FTIR spectroscopy can be accomplished in a few minutes and works with almost any substrate. FTIR equipment is relatively low cost and easy to operate and maintain. The method was validated by correlating FTIR results with migration testing on EB coatings cured with a series of dose levels.

## Introduction to UV/EB Chemistry

The chemistry of UV and EB coatings, hereafter collectively referred to as radiation-curable coatings, is dominantly based on monomers and oligomers containing acrylate end groups. The vinyl moiety of these acrylate groups undergoes a free radical polymerization upon exposure to radiation. A UV system requires a photoinitiator that forms a free radical species upon exposure to UV energy while an EB system uses high-energy electrons to irradiate the coating. Monomers and oligomers can contain multiple acrylate end-groups resulting in polymers with a high cross-link density.

Upon cure, radiation-curable coatings provide various desirable surface qualities to packaging including protection of inks, a range of gloss levels, and tactile effects like a soft feel. These coatings are applied to various types of packaging including folding cartons, labels, multi-wall bags, and flexible packaging. Printing

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and application technologies of radiation-curable coatings include narrow web flexography, wide web central impression flexography, sheet-fed offset, and web offset. Radiation-curing technology is also used for digital printing including inkjet inks and over print varnishes (OPVs) to protect dry and liquid electrographic toner based printing systems. Furthermore, UV/EB chemistry has applications beyond OPVs and inks on packaging, these include laminating adhesives, protective coatings for flooring and furniture, and ink receptive primers for various forms of printing.

The extent of acrylate polymerization greatly affects the final performance properties of radiation-curable coatings. Consequently, coatings are formulated to work within a narrow range of radiation doses. If a radiation-curable coating does not receive the appropriate exposure to UV or EB energy, whether it be too much or too little, the final product will not meet the required specifications. For example, a weather-resistant protective top coat requires the coating to be highly polymerized and cross-linked in order to achieve functional inertness. Conversely, a pressure-sensitive adhesive requires cure parameters to achieve low levels of cross-linking in order to optimize both the shear and tack properties of the adhesive.

## Introduction to Food Packaging Regulations

There is a developing market for radiation-curable coatings on food packaging especially as OPVs over digital inks on flexible packaging. Radiation cured coatings are generally not suited for direct food-contact; however, current regulations permit indirect food-contact which means these types of coatings can be applied to the non-food contact side of a food package. The US FDA requires that acrylated monomers and oligomers used on a food package be undetectable in the food using an analytical methodology with a minimum sensitivity of 50 ppb (w/v) [1]. In 2008 the FDA issued Food Contact Notification (FCN) 772 allowing specific acrylate monomers to have a detected migration level of up to 1 ppm (w/v) in food [2].

Certain types of packaging materials such as glass and aluminum foil are regarded as functional barriers. In these cases, migration testing is not required since the package itself is considered impervious to migration [3]. However, most flexible packaging materials are not deemed a functional barrier, and migration testing is required to validate that the non-food safe packaging components are not leeching into the food. Additionally, functional barriers may prevent migration, but set-off is still a possibility. Set-off occurs when the coating transfers to the food-contact side of a package while the unfinished packaging is in a roll or stack during processing. This is in contrast to migration which occurs when the components of the finished package migrate through the packaging structure into the food.

The EU has stricter migration limits than the US. Again, acrylate monomers and oligomers must remain undetectable, but the required analytical sensitivity in the

EU is 0.01 mg/kg (10 ppb) or less [4]. Additional food-packaging regulations include the commonly referenced "Swiss List," which is considered a positive list of materials permitted on a food package [5]. The Swiss List allows specific acrylate monomers in concentrations of 0.01 or 0.05 mg/kg (10 or 50 ppb, respectively).

The US FDA and the EU have published standardized protocols for the migration testing of food packaging [6][4]. The two main considerations of a migration test are the choice of food simulant and incubation conditions. The simulant is chosen based on food-type, i.e., fatty, acidic, alcoholic, etc. Incubation conditions are selected based on the storage temperature and end-use temperature of the food as well as the temperature of the food upon filling the package. The food package is mounted in a migration cell with the simulant exposed to the food-contact side of the package. The recommended simulant volume to food package area is 10 mL per in2. This ratio is based on the assumption that 10 g of food will be in contact with 1 in2 of packaging. The filled migration cell is then incubated according to the prescribed conditions. The minimum incubation duration is 10 days.

## Ensuring Low-Migration of UV/EB Coatings

In order to maintain radiation-curable coating components as undetectable, these coatings must be adequately polymerized. The materials originating from the radiation-curable coatings that are available for migration include any residual, unreacted acrylate monomers and oligomers. These residual monomers and oligomers are not bound to the polymeric matrix and, consequently, are available to move, whether it be through migration or set-off. However, as described previously, a functional barrier prevents migration, making set-off the more likely phenomenon leading to the detection of acrylated materials in food.

The current industry protocol to ensure food packaging is safe entails employing a third-party lab to perform migration testing on a finished package. However, this validation process is slow, especially considering that the migration tests alone require a minimum incubation of 10 days. This type of testing is also expensive meaning that it is unsustainable for a packaging converter to validate each production job of package intended for food. This leaves the converter in a high-risk position where there is a potential for an unsafe food package to reach the consumer.
Implementing a quality control method for the package converting process is very desirable to ensuring food packaging using radiation-curable coatings meet the regulatory requirements and are safe for use. However, the instruments typically used in a migration test are expensive, tedious, and require special training to properly utilize. Such analytical instruments and techniques include gas-chromatography (GC) or high-performance liquid chromatography (HPLC), either ideally with mass spectrometry (MS) capabilities.

Fourier transform infrared spectroscopy (FTIR) with an attenuated reflectance (ATR) crystal is an ideal candidate for quality control. It is relatively inexpensive with regard to both its initial investment cost and routine maintenance requirements. A diamond or zinc selenide (ZnSe) ATR crystal is well-suited for analyzing surface coatings, such as radiation-curable coatings, due to the average depth of penetration being two microns. Furthermore, there is no sample preparation, and the FTIR analysis is non-destructive. Macros programmed into the FTIR's software make quality control assessment straight-forward with nearly instantaneous results.
FTIR can monitor the extent of acrylate polymerization of a radiation-curable coating. Absorbance at 810 cm-1 constitutes a C-H out-of-plane bending of an acrylate's vinyl group. As the acrylate polymerizes, the vinyl group disappears along with absorbance at 810 cm-1. By comparing the normalized area of the uncured, liquid radiation-curable coating to that of the cured coating, the extent of acrylate polymerization can be expressed as a percentage.

By comparing and correlating the extent of acrylate polymerization determined by FTIR to the amount of potential acrylate migrants established through GCMS analysis, quality control with FTIR becomes a powerful and rapid method to ensure radiation-curable coatings are appropriately cured and comply with migration regulations.

**FTIR Experimental Procedure**

Unprinted polyester/polyethylene laminate flexible packaging films were coated with an EB coating on the film's polyester side. These films were cured with an electron beam at various doses and speeds as described in Table 1 below. The oxygen levels remained consistent for each sample at less than 200 ppm. The films were received in 11 separate rolls for testing.

Three samples from each film roll were analyzed in triplicate (n=9) using a Bruker ALPHA-P FTIR spectrometer with a diamond ATR crystal at a 4 cm-1 resolution. The uncured coating (n=3) was also analyzed. The spectra were manipulated and evaluated using Bruker's OPUS software.

The relative extent of acrylate polymerization can be quantified by monitoring the disappearance of a vinyl group's C-H out-of-plane bend at 810 cm-1. Percent 810 cm-1 area decrease was calculated by first normalizing each spectrum on the carbonyl stretching frequency using a min-max algorithm. Absorbance at 810 cm-1 was integrated and averaged for each replicate spectra to determine peak area. The percent 810 cm-1 area decrease was determined from comparison of the films' averaged absorbance integral to the averaged absorbance integral of the uncured coating using the following equation:

$$\% \text{ Area Decrease} = \frac{\text{Initial}_{810} - \text{Final}_{810}}{\text{Initial}_{810}} * 100 \quad (1)$$

where "Initial" is the absorbance integral of the uncured coating at 810 cm-1 and "Final" is the absorbance integral of the polymerized coating at the same frequency.

| *Film Sample* | *Speed (m/min)* | *Dose (kGy)* |
|---|---|---|
| *1* | 20 | 20 |
| *2* | 20 | 30 |
| *3* | 20 | 40 |
| *4* | 80 | 20 |
| *5* | 80 | 30 |
| *6* | 80 | 40 |
| *7* | 90 | 20 |
| *8* | 90 | 30 |
| *9* | 90 | 40 |
| *10* | 97 | 20 |
| *11* | 97 | 40 |

***Table 1.*** *Description of tested film samples.*

**GCMS Validation Procedure**

The GCMS analysis on a Shimadzu GCMS-QP2010 Plus with an AOC-20i auto injector was optimized for the detection of two different acrylated monomers (M1 and M2) and butylated hydroxytolune (BHT), the internal standard. The column was a 30-m Rtx-5MS and parameters included a 2 µL splitless injection. Helium was used as the carrier gas. The column's flow was controlled via pressure at 65 kPa, and the starting temperature was 100°C. The mass detector was set to scan only for ions that corresponded to the three chemicals of interest. This optimized GCMS program was used for the entirety of the study. Peaks were integrated using Shimadzu's LabSolutions software.

Standards containing M1, M2, and BHT all at the same concentration were analyzed with GCMS to generate linearity curves (Figure 1). A range of concentrations between 0.15 and 4 ppm (w/v) was evaluated. One major ion for each chemical was selected for data analysis. These ions were chosen because they were: 1) specific to the chemical; 2) demonstrated linearity; and 3) maintained consistent response factors across the concentration range.
Standard solutions of M1 and M2 at known concentrations (0.01, 0.1, 0.5,

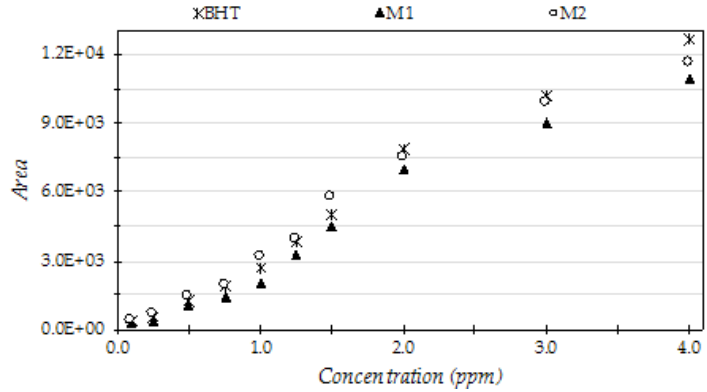


***Figure 1.*** *Linearity curves of BHT, M1, and M2 at various concentrations with R2 values of 0.98, 0.97, and 0.97, respectively.*

1.0, and 2.0 ppm (w/v)) in 250 mL 95% ethanol were spiked with 250 ppb (w/v) BHT and concentrated to approximately 5 mL with a rotary evaporator. The concentrates were analyzed with GCMS and modeled in Figure 2. The trend lines of M1 and M2 are y = 1.50x + 0.04 (R2 = 0.99) and y = 0.84x – 0.03 (R2 = 0.98), respectively. This model was used as a correction method for the calculation of analyte concentration.

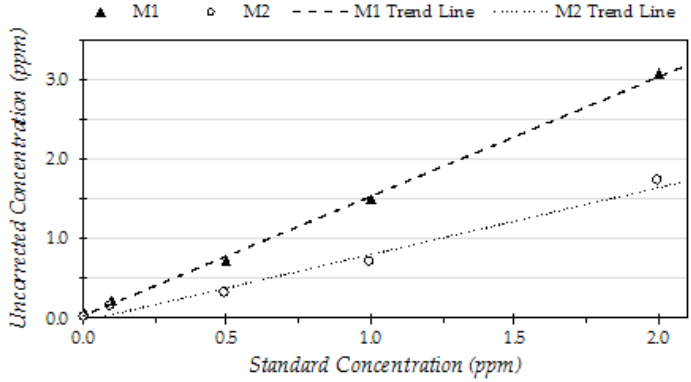


***Figure 2.*** *Calibration model of M1 and M2 at various concentrations using BHT as an internal standard.*

## Extraction and Migration Testing Procedures

The 11 film samples used in the FTIR analysis underwent a total extraction where the samples were cut into 25 in2 samples, separately introduced into 250 mL of 95% ethanol, and shaken in closed flasks for 48 hours. A blank containing a sample of uncoated film was assessed using the same procedure.

Migration testing following FDA protocols for fatty foods under Condition of Use B (boiling water sterilized food-fill; room temperature storage) was completed on

three of the supplied film samples (films 3, 6 and 7) by exposing the food-contact side of the film to 95% ethanol simulant. A blank using uncoated film was included in the migration testing. These samples were sealed in a migration cell that exposes 24 in2 of the films' surface to the simulant. The cells were filled with 240 mL 95% ethanol to maintain a 10 mL/in2 ratio of simulant volume to surface area as recommended by the FDA. The migration cells were incubated for 2 hours at 100°C followed by 10 days at 40°C.

An additional migration test was completed using the FDA protocol for fatty foods under Condition of Use E (room temperature food-fill and storage). Films 3 and 6 and a blank using uncoated film were included in this testing. The migration cells were incubated at 40°C for 10 days. The setup of the migration cells followed the same method as described above for the Condition of Use B migration testing.
Each sample from the total extraction and the migration testing was spiked with 250 ppb (w/v) BHT upon completion of the allotted time period and concentrated to approximately 5 mL using a rotary evaporator. The concentrates were analyzed with the GCMS program described earlier, and the chromatograms were assessed and quantified in the same manner as the standards.

## Results and Discussion

There is a clear predictive relationship between FTIR analysis of the coated films and the amount of potential extracted acrylate monomers as quantified through GCMS. This correlation is graphed in Figure 3. The formula of the trend line is $y = 4\,561x - 408$ ($R^2 = 0.91$). A natural log fit was chosen since the extent of acrylate polymerization does not reach 100% due to steric hindrance from the decreasing mobility of the polymer matrix.

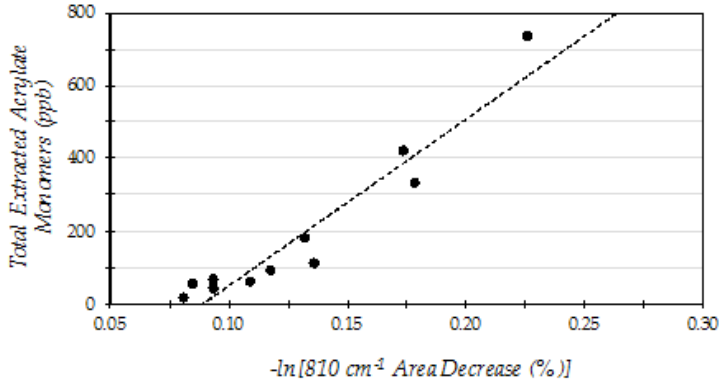


***Figure 3.*** *Relationship between total extracted acrylate monomers and 810 $cm^{-1}$ area decrease.*

The amount of acrylate extractables as quantified through GCMS analysis compared to the extent of acrylate polymerization as determined with FTIR is tabulated in Table 2. The amount of acrylate material detected after the two migration tests is shown in Table 3. Comparing the amount of acrylate material detected from the total extraction against the data from the migration tests indicates that the flexible packaging structure is acting as a barrier for the M2 monomer. However, M1 is either a migrant or highly susceptible to set-off as the total extraction method accurately predicts the amount of M1 present in the simulant after a migration test. In order to determine if M1 is a true migrant, further testing using film not wound in a roll is required. Additionally, the flexible packaging structure appears vulnerable to increased temperature: migration testing using condition of Use B (boiling water fill) shows greater amounts of M2 compared to Condition of Use E (room temperature fill). Overall, the total extraction accurately represents a worst-case-scenario prediction of either tested migration condition.

| *Film Sample* | *M1 (ppb)* | *M2 (ppb)* | *810 $cm^{-1}$ Area Decrease* |
|---|---|---|---|
| *1* | 35 | 73 | 87.2% |
| *2* | 7 | 28 | 91.0% |
| *3* | 3 | 8 | 92.1% |
| *4* | 121 | 206 | 83.6% |
| *5* | 28 | 29 | 89.6% |
| *6* | 13 | 37 | 91.8% |
| *7* | 196 | 218 | 84.0% |
| *8* | 44 | 132 | 87.5% |
| *9* | 15 | 51 | 91.0% |
| *10* | 284 | 442 | 79.7% |
| *11* | 23 | 68 | 88.8% |

***Table 2.*** *Total extraction results compared to the determined extent of acrylate polymerization.*

| | *Condition of Use B (Boiling water fill)* | | *Condition of Use E (Room temp. fill)* | |
|---|---|---|---|---|
| *Film Sample* | *M1 (ppb)* | *M2 (ppb)* | *M1 (ppb)* | *M2 (ppb)* |
| *3* | 5 | 3 | 5 | 0 |
| *6* | 11 | 7 | 11 | 1 |
| *7* | 206 | 57 | - | - |

***Table 3.*** *Migration results.*

## Conclusions

While FTIR cannot fully replace a true migration test, quality control through FTIR can reliably predict the potential amounts of migrants originating from a radiation-curable coating. Implementing a press-side quality control check with FTIR reduces packaging converter risks and is an excellent tool for use in a Good Manufacturing Practices (GMP) program. The FTIR method is rapid, with results available within minutes of each finished job. The initial investment cost of the FTIR should be offset by product-loss prevention and by reducing the use of third-party labs for migration validation.

Furthermore, quality control with FTIR can be used for all types of radiation-curable coatings and has use for many products beyond food packaging. Since the extent of acrylate polymerization can affect the performance properties of the final product, a quality control check using FTIR confirms the radiation-curable coating is polymerized within the required specifications. Again, the benefits of utilizing a rapid quantitative analysis to verify the extent of acrylate polymerization is quickly realized.

## Ongoing and Future Work

Current research focuses on the development of a quality control method to monitor the cure of radiation-curable coatings in real time using Fourier transform near infrared spectroscopy (FT-NIR). Quality control with FTIR requires that the production job be finished before validation. With FT-NIR, a process probe is mounted directly on the press for non-contact analysis of the cured coating as the product is still being processed. Real-time measurements would alert press operators to issues as they occur, further decreasing the potential for product-loss by increasing control over production conditions and GMP programs.

## Bibliography


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