

Electron Beam Curing Properties of Water Based Monomer and Polymer Materials

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Abstract

The electron beam (EB) curing properties of acrylate functional monomer/water solutions and polyurethane dispersions (PUDs) in water were characterized. Many of the materials showed good curing properties by EB alone without prior thermal drying. Gravimetric analysis showed effective removal of water from the films even at dose levels as low as 10 kGy. Many of the materials also showed excellent resistance to isopropyl alcohol after curing at low dose levels. The conversion of acrylate functional groups was characterized by FTIR. Potential advantages of water based EB curing systems include safe handling, low viscosity, low odor, low migration, and curing without added thermal drying.

Introduction

The basic building blocks of UV/EB curable formulations are acrylate functional monomers and oligomers. A common formulating strategy is to select oligomers based on the desired cured coating physical properties. Monomers serve as reactive diluents to control the viscosity of the formulations. This strategy works well except when the desired application method requires very low viscosity. This may be the case for spray coating, vacuum coating, inkjet, or gravure printing methods. In order to achieve very low viscosity a formulation may have high monomer content with very little allowance for oligomers. High monomer content may reduce curing speeds and may limit the physical properties of the resulting cured films. Also, from a health and safety perspective, it may not be desirable to spray formulations based on low molecular weight monomers.

An alternate method to reduce viscosity is to use water as a diluent in place of monomers. In this case specialized acrylate functional monomers or oligomers may be used which are soluble or may be dispersed or emulsified in water.¹ Acrylate functional polyurethane dispersions (PUDs) are well known and have become well established in commercial sprayable, UV curable finishes for wood.² The main disadvantage of water based UV curable materials is that two drying steps are needed: an initial thermal drying to remove water, followed by UV curing to further polymerize and crosslink the coating.

The UV curing properties of water based acrylate functional materials have been widely studied and reported; however, very little is known about the EB curing properties of these materials. A US patent reference discloses EB curable compositions containing water. After EB curing the formulations showed low migration of monomers that were used in the formulations.³ Another patent discloses a flexographic ink system where partial evaporation of water from the ink causes a viscosity increase that allows wet-trapping of multiple ink layers followed by EB curing after the last ink layer is applied.⁴ Water based materials were also used to develop EB curable gravure ink systems.⁵

The purpose of this study is to characterize the EB curing properties of acrylate functional monomer/water solutions and PUDs. The results may be used as a basis for exploring new applications for this technology.

Experimental

Commercial raw materials were used as received. Mixtures were prepared by weighing and hand-stirring the raw materials. Viscosities were measured at 25°C using a Brookfield DV-E viscometer equipped with small sample adapter (s34 spindle) at 50 or 100 rpm.

Coated samples were prepared by draw-down with a #8 wire-wound rod on sheets of 50 micron polyester (PET) film. Coatings were cured immediately after draw-down using a Comet EBLab 200 system operating at 125 kV with an atmosphere of less than 200 ppm O₂. Samples were placed in the sample tray which was run a speed of 18 m/min under the beam. The EBLab system automatically adjusts beam current to provide the desired dose set point.

Coating weights were determined by marking a (2.5 x 3 inch) area on PET film. The mass of the film and coating were determined (+/- 0.0005 g) after EB curing. The dry weight of coating was determined by removing coating and subtracting the weight of the film. It was difficult to measure weight of the coating before curing since the water would begin to evaporate from the thin film immediately after coating. For the monomer samples a reference wet coating weight was determined using the monomer without added water. For the PUD samples a reference wet weight of 0.0545 grams (for the 2.5 x 3 inch area) was used. This was determined using a 100% solids non-volatile material (Sartomer SR9020) applied with a #8 wire-wound rod. Weight loss was determined by subtracting the coating weight after curing from this reference wet coating weight.

The curing properties of the coatings were characterized by rub testing. Four layers of paper towels were wrapped on the round end of a 1 kg ball-peen hammer. The coating was examined after ten back-and-forth strokes of the dry paper towel surface on the coating under the weight of the hammer. The same test was then repeated using paper towel layers that were saturated with isopropyl alcohol (IPA). The effect of dry and IPA rubs on the coatings were ranked on the following scale:

- 0 – No cure/complete removal of coating
- 1 – Tacky coating/severe smudging
- 2 – Significant effect from rub test
- 3 – Slight effect from rub test
- 4 – No visible effect from rub test

Rub testing was also conducted after thermal drying for 3 min at 80° C in a convection oven without EB curing.

Samples for FTIR conversion measurements were prepared by draw-down with a #8 wire-wound rod on 90 micron low density polyethylene film. The coated side of the film was clamped in a reflectance (ATR) cell of a Thermo Nicolet Nexus 670 FTIR spectrometer. The samples were analyzed with a 4.0 cm⁻¹ resolution and a 1.2 second scan time. The amount of unreacted acrylate was quantified using the 810 cm⁻¹ peak from C-H out-of-plane bending from the acrylate vinyl group. Absorbance was measured from the baseline of the peak and then normalized to the carbonyl peak at 1730 cm⁻¹. Conversion was

determined by the ratio to the 810 cm^{-1} absorbance for the uncured material. A well type ATR cell was used for materials that were liquid before EB curing.

Web coating and curing tests were run on the EB pilot line at PCT Engineered Systems. Coatings were applied to 50 micron PET using an offset gravure coater equipped with a 130 line/inch, 15.7 BCM gravure roll. This configuration produced a wet coating weight of about 6.0 g/m^2 . Immediately after coating the web entered a BroadBeam EP series curing unit operating at 150 kV under a nitrogen (<200 ppm O_2) atmosphere.

Results and Discussion

Water Soluble Monomers

Four different water soluble monomers were investigated (Table 1). Monomers A, B, and C are water soluble by virtue of the high degree of ethoxylation. Monomer D is water soluble due to the hydrophilic nature of the two secondary hydroxyl groups. The chemical structure of monomer D is shown in Figure 1. All four monomers were completely miscible and stable in mixtures with up to 30 percent water. The viscosities of the monomers as a function of added water is shown in Figure 2. A more rapid reduction of Monomer D viscosity relative to the other monomers was observed.

Table 1. Water Soluble Acrylate Functional Monomers

	Monomer	Trade Name	Functionality	Average Mwt
A	PEG(400 mw) diacrylate	Sartomer SR344	2	400
B	EO(30)Bisphenol-A diacrylate	Sartomer SR9038	2	1656
C	EO(15) trimethylolpropane triacrylate	Sartomer SR9035	3	956
D	Butanediol diglycidylether diacrylate	Laromer LR8765R	2	346



Figure 1. Chemical structure of Monomer D.

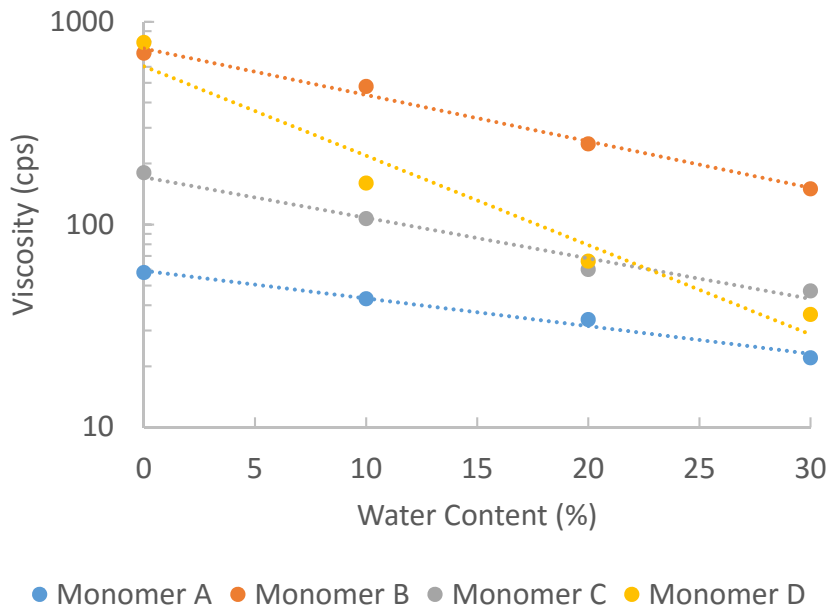
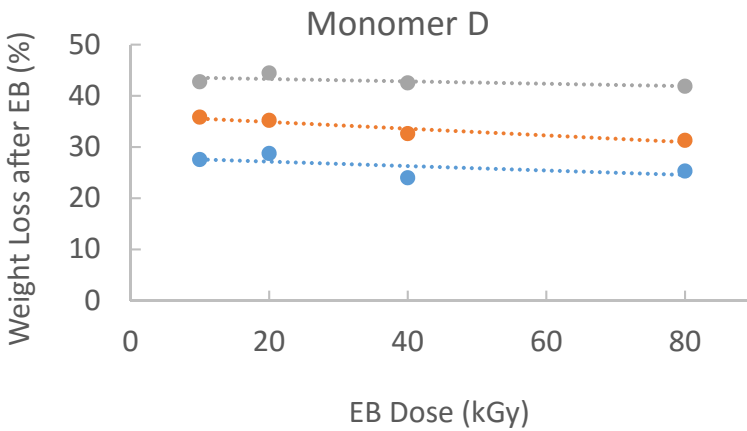
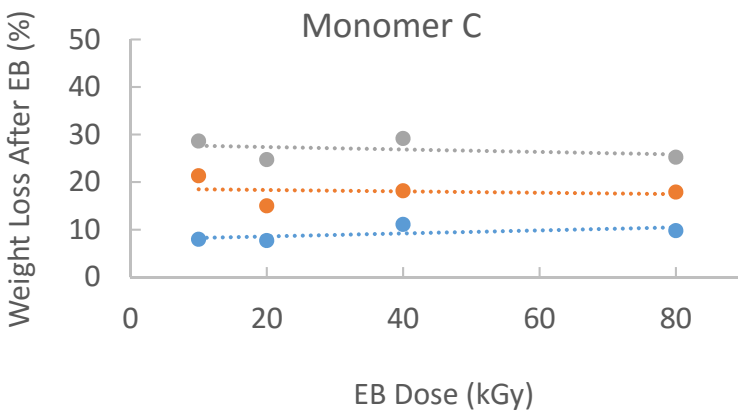
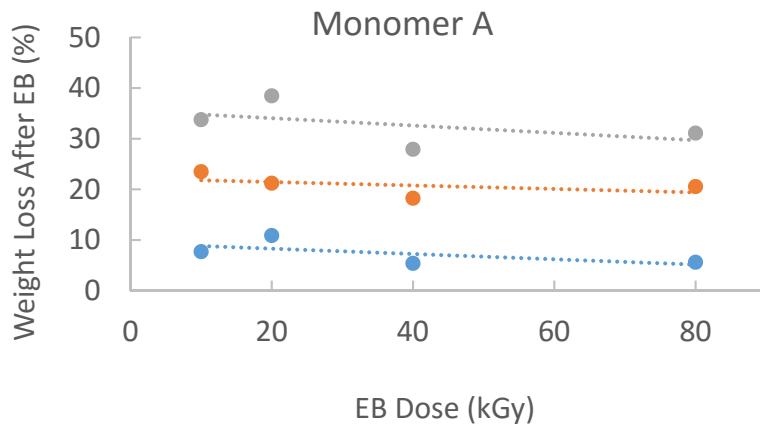


Figure 2. Viscosity of monomer/water mixtures.

Figure 3 shows the weight loss for monomers A, C, and D after EB curing at 10, 20, 40, and 80 kGy. It was interesting to see that the weight loss corresponded closely to the amount of added water indicating that water was completely eliminated from the coating even without any prior thermal drying. In addition, this weight loss occurred even at lowest (10 kGy) EB dose level.

Figure 4 shows the IPA rub resistance of the monomer series as a function of the amount of added water using a constant 40 kGy EB dose level. The IPA resistance of monomers A, B, C was poor even in the absence of water. This was not surprising due to the relatively low amount of crosslink density corresponding to the high level of ethoxylation. The most interesting monomer in this series was D, which had excellent IPA resistance with and without added water.

Figure 5 shows the IPA rub resistance of the monomer series as a function of EB dose for mixtures with 20 percent water. Again, monomers A, B, and C show poor IPA resistance due to the high levels of ethoxylation and do not result in a significant change in IPA resistance even with dose levels up to 80 kGy. Again, monomer D is very interesting here showing excellent IPA resistance with a dose level of only 10 kGy.



- 90/10 Monomer/Water
- 80/20 Monomer/Water
- 70/30 Monomer/Water

Figure 3. Weight loss of monomer/water solutions after coating and curing.

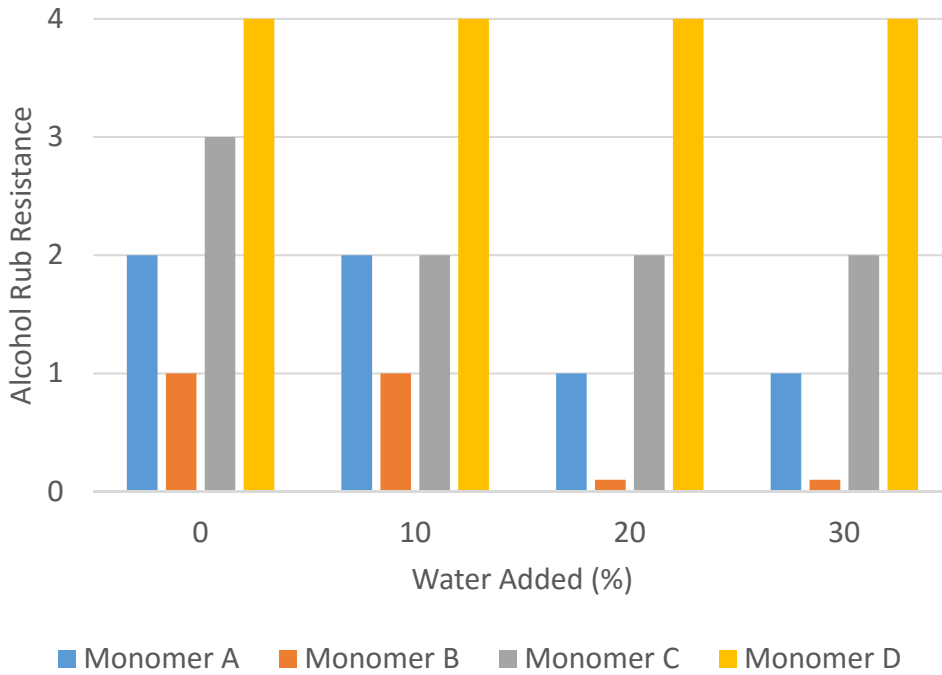


Figure 4. Alcohol rub resistance of monomer/water mixtures after coating and curing at 40 kGy (0 = complete removal of coating, 4 = no visual effect).

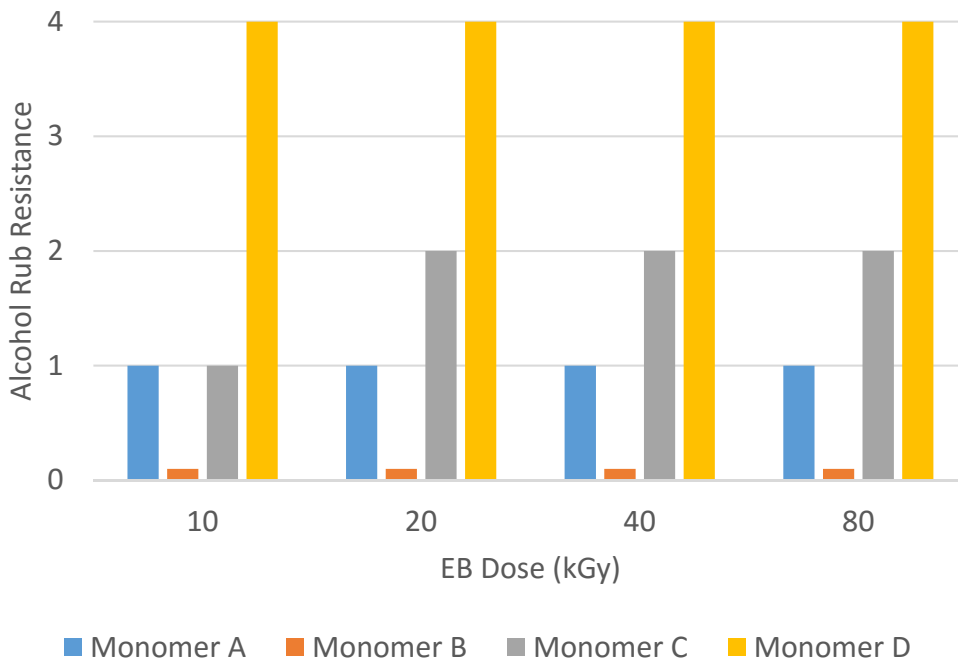


Figure 5. Effect of EB dose on alcohol rub resistance of coatings formed from 80/20 monomer/water mixtures (0 = complete removal of coating, 4 = no visual effect).

Acrylate Functional PUDs

Sixteen different commercial acrylate functional PUDs were investigated (Table 2). Information available from the suppliers indicated solids levels ranging from 35 to 65 percent for these materials. The weight losses of these materials were determined after EB curing at 10 to 80 kGy. Representative plots of the weight losses for PUDs 9 and 16 are shown in Figure 4. Results were similar to monomers in that weight loss was constant over this dose range. The average weight losses for all dose levels for all 16 PUDs are shown in Table 2. The results closely compliment the solids levels given by the manufacturers. This indicates that all of the water is removed by EB curing even without any additional thermal drying. Furthermore, the water is removed at dose levels as low as 10 kGy.

Table 2. Acrylate Functional Polyurethane Dispersions and Weight Losses after EB Curing

Polymer	Trade Name	Solids (%)	Weight loss after EB (average of 10, 20, 40 and 80 kGy samples, %)
PUD 1	Alberdingk resin	39	66
PUD 2	Alberdingk resin	45	59
PUD 3	Alberdingk resin	40	69
PUD 4	Alberdingk resin	35	76
PUD 5	Alberdingk resin	40	64
PUD 6	Ucecoat 6558	50	41
PUD 7	Ucecoat 7200	65	42
PUD 8	Ucecoat 7571	35	67
PUD 9	Ucecoat 7655	35	69
PUD 10	Ucecoat 7674	40	62
PUD 11	Ucecoat 7689	35	70
PUD 12	Ucecoat 7699	35	77
PUD 13	Ucecoat 7710	45	57
PUD 14	Ucecoat 7718	40	61
PUD 15	Ucecoat 7734	38	63
PUD 16	Ucecoat 7856	45	58

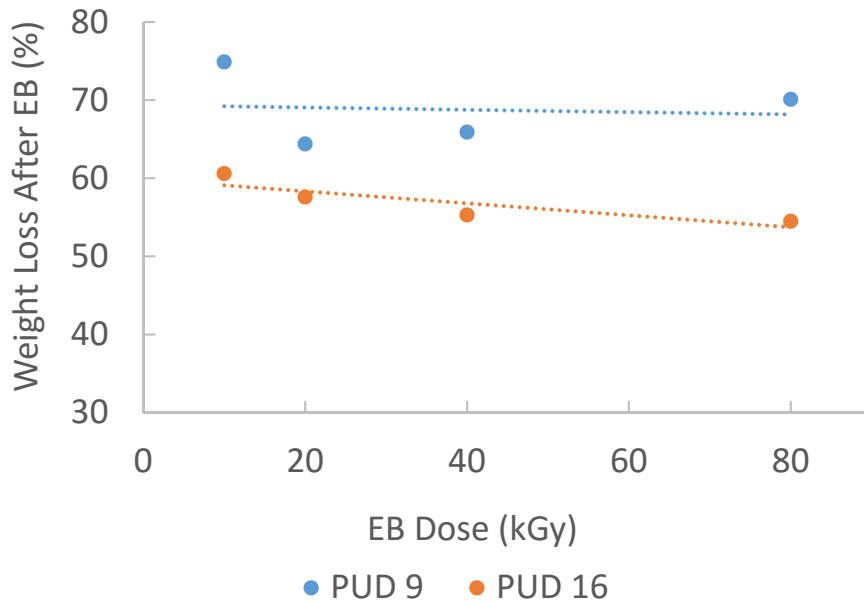


Figure 6. Weight loss of PUDs after coating and curing.

Table 3 shows the EB curing properties of the PUDs characterized by the dry and IPA rub resistance of the resulting coatings. Some PUDs are designed to give tack-free dry coating layers upon evaporation of water even before curing. This is beneficial for some wood coating applications where it may be desirable to repair the coating layer before crosslinking. PUDs 3, 4, and 8 from this study form tack-free films that are resistant to dry rubs even before EB curing. The low IPA resistance of these materials indicates they do not crosslink without EB curing. A comparison of the IPA rub results before and after EB exposure indicates that all 16 of the PUDs are crosslinked by EB. Most of the PUDs show some increase in IPA resistance between 10 and 40 kGy. Many of the materials were completely resistant to damage by 10 IPA rubs after 40 kGy.

Mixtures of PUDs with monomer C (70/30) were prepared to check for synergistic effects on the curing properties. It was noted that many of the mixtures were not compatible (Table 4). This was indicated by a phase separation immediately upon mixing or sometime after mixing the materials. Even if phase separation did occur, the samples were remixed, drawn-down, and EB cured to check for IPA rub resistance. Many of the mixtures did show an enhancement in the IPA rub resistance after 10 and 40 kGy (compare Tables 3 and 4).

Table 3. EB Curing Properties of Acrylate Functional Polyurethane Dispersions

Polymer	Dry rub resistance			IPA Rub Resistance		
	No beam	10 kGy	40 kGy	No beam	10 kGy	40 kGy
PUD 1	0	4	4	0	2	4
PUD 2	0	4	4	0	1	4
PUD 3	4	4	4	1	1	4
PUD 4	4	4	4	1	1	4
PUD 5	0	4	4	0	4	4
PUD 6	0	3	3	0	1	2
PUD 7	0	4	4	0	1	3
PUD 8	3	3	4	1	1	2
PUD 9	2	4	4	1	1	4
PUD 10	0	4	4	0	1	3
PUD 11	2	3	4	1	1	3
PUD 12	2	3	4	1	1	4
PUD 13	0	4	4	0	1	4
PUD 14	0	4	4	0	2	4
PUD 15	2	4	4	1	1	2
PUD 16	0	4	4	0	2	4

Table 4. Compatibility and Curing of 70/30 PUD/Monomer C Mixtures

Polymer	Compatibility upon mixing	Compatibility after 2 weeks	IPA rub resistance	
			10 kGy	40 kGy
PUD 1	yes	yes	3	4
PUD 2	no	no	2	3
PUD 3	no	no	4	4
PUD 4	yes	no	4	4
PUD 5	yes	no	4	4
PUD 6	yes	yes	1	1
PUD 7	no	no	3	4
PUD 8	yes	yes	2	4
PUD 9	yes	yes	4	4
PUD 10	yes	no	3	4
PUD 11	yes	yes	1	4
PUD 12	no	yes	3	4
PUD 13	yes	no	3	4
PUD 14	yes	no	2	3
PUD 15	no	yes	4	4
PUD 16	yes	no	4	4

Characterization of Curing by FTIR Analysis

The EB curing properties of the acrylate functional monomer/water solutions and polyurethane dispersions (PUDs) in water as characterized by weight loss and rub resistance were impressive. FTIR analysis was also used to get a direct measure of the actual conversion of acrylate groups in the EB curing process. The FTIR spectra at varying cure doses for 80/20 monomer C/water is shown in Figure 7. The spectra for PUD 5 at varying cure doses is shown in Figure 8. The characteristic 810 cm^{-1} peak of the acrylate group was used for quantification.

Figure 9 shows the acrylate group conversion for monomers A, C and D as a function of EB dose. It is interesting to note that all three of these monomers give more than 97 percent conversion at dose levels as low as 20 kGy. This high conversion may be due to the presence of water in the early stages of the curing which may enhance the mobility of the acrylate end-groups.

Figure 10 shows the acrylate group conversion for many of the PUDs. The results show rapid conversion after 10 to 20 kGy with a gradual increase in conversion up to 80 kGy. The conversion for PUDs ranges from about less than 60% to more than 90% depending on the PUDs that were used.

Note, conversion data for monomer B and some of the PUDs are missing from Figures 7 and 8. This is due to interfering bands around 810 cm^{-1} in the FTIR spectra that make it difficult to quantify the conversion.

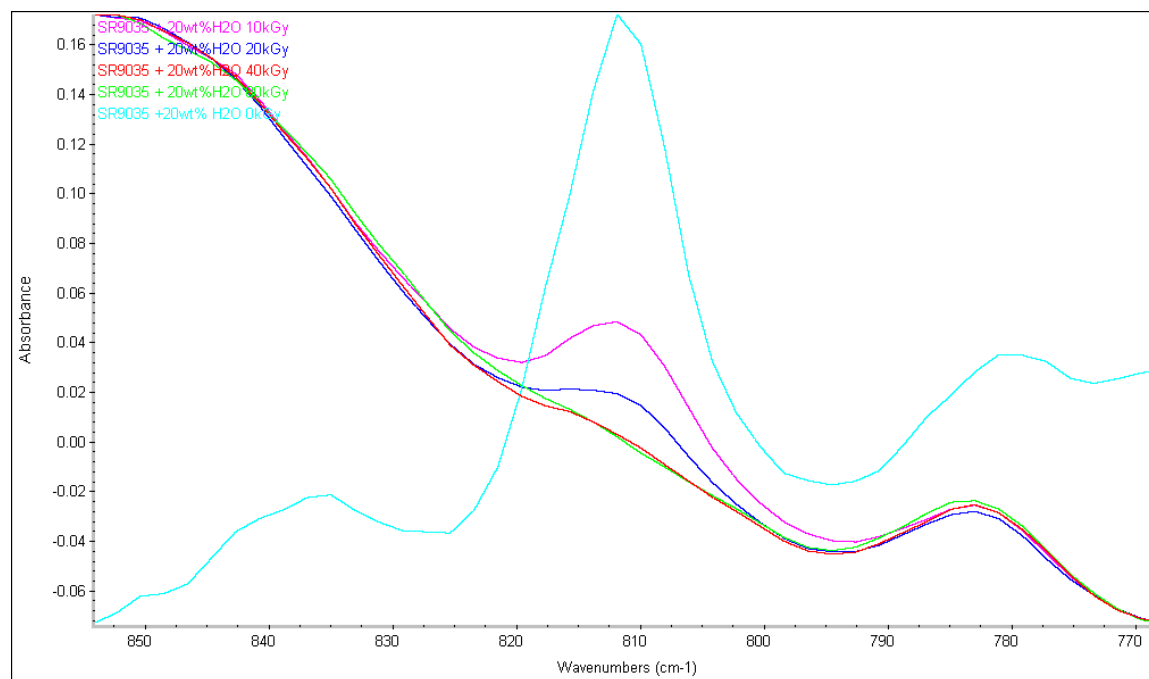


Figure 7. ATR spectra of 80% monomer C/ 20% water mixtures after EB at 0, 10, 20, 40, and 80 kGy dose levels.

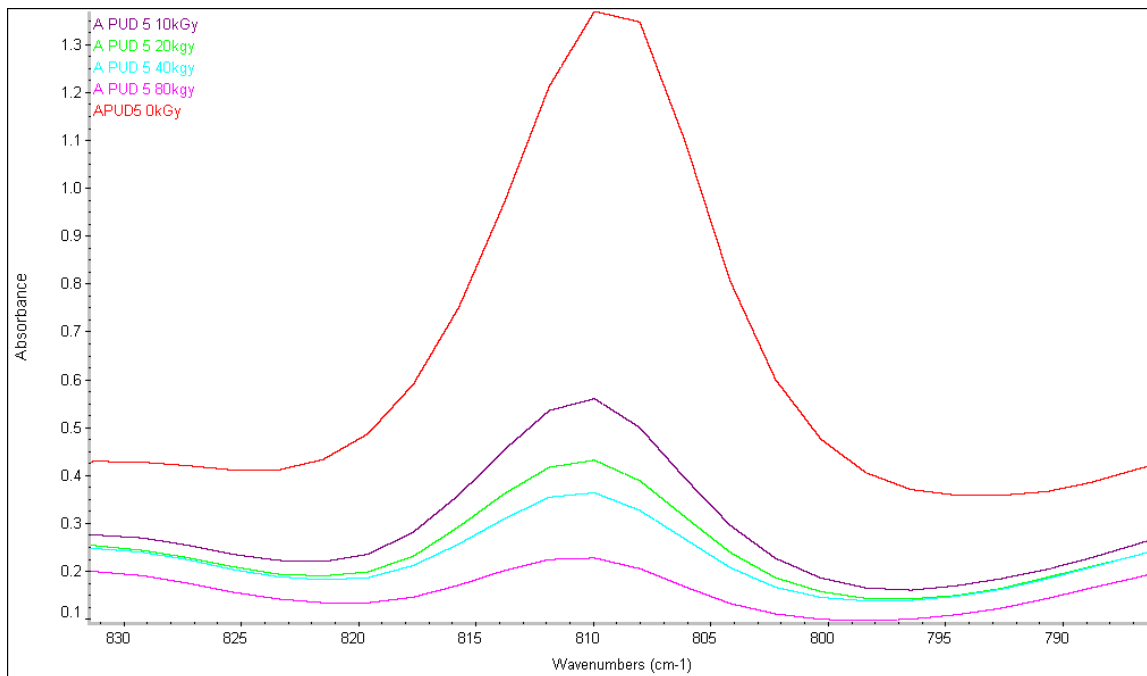


Figure 8. ATR spectra of PUD 5 after EB at 0, 10, 20, 40, and 80 kGy dose levels.

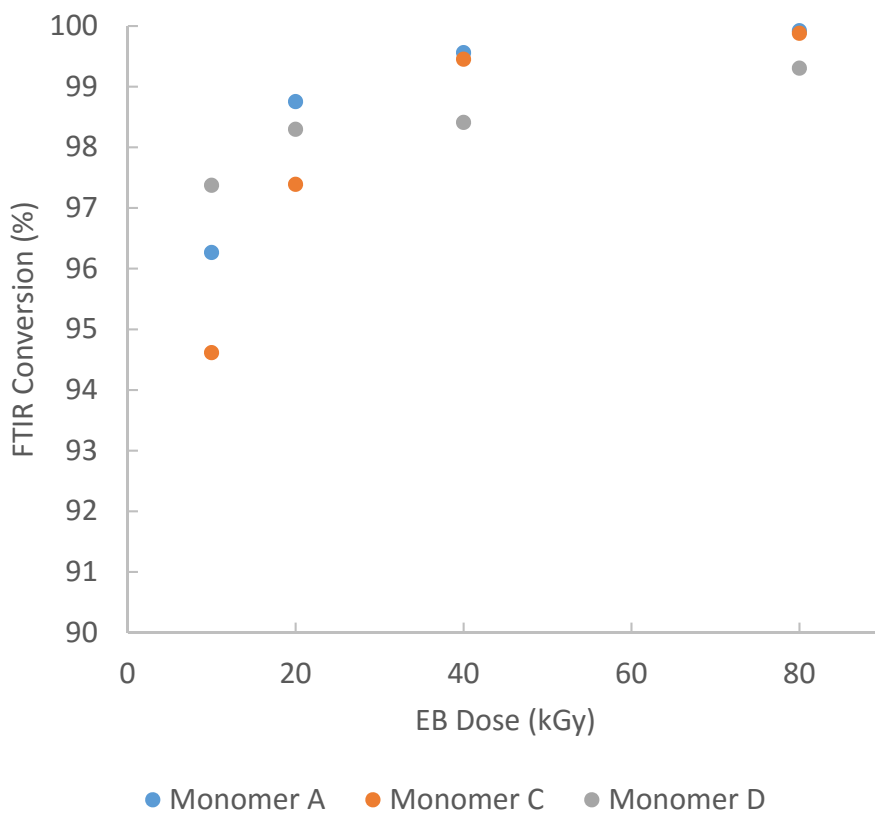


Figure 9. FTIR Conversion of 80/20 monomer/water mixtures as a function of EB dose.

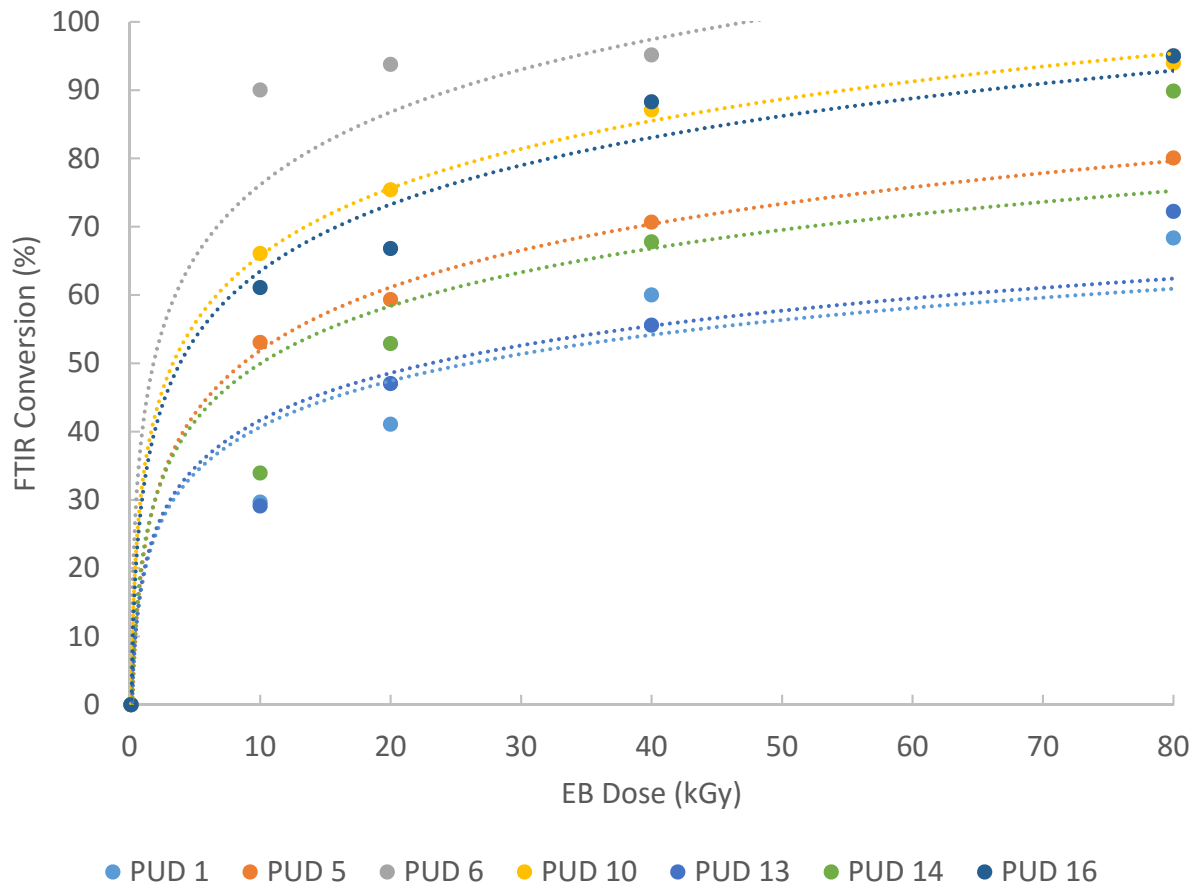


Figure 10. FTIR Conversion of PUDs as a function of EB dose.

Web Coating and Curing

The results of the laboratory EB curing of cut sheet samples indicate that evaporation of water and EB crosslinking can occur in a single step. Because of the time delay between coating draw-down and cure (about 30 seconds) there was some concern that some evaporation of water may have occurred at room temperature during this delay period. In order to test the feasibility of a single EB drying step, web coating trials were conducted. In this study the coater was located immediately before the EB system to minimize any ambient drying that may occur. PUDs 2, 4, 5 along with 70/30 monomer D/water were tested in this manner. In one sequence of tests these four materials were coated (about 6 g/m² wet) at 50 ft/min. The dose level was started at 80 kGy and sequentially lowered to 40, 20, 10, and 0 kGy while continually checking for coating that was cloudy, wet, or easily scratched at the exit of the EB system. Surprisingly, coatings from all four materials were clear, dry, and scratch resistant even as low as 10 kGy. At 0 kGy (beam off), as expected, the coatings were wet and milky upon exit from the EB system.

In a second sequence of tests the dose was maintained at 40 kGy and the line speed was sequentially increased in 50 ft/min increments up to 250 ft/min. The results summarized in Figure 11 show that PUD 5 was wet at 100 ft/min while PUD 2 and 4 remained dry up to 150 ft/min. The monomer D/water (70/30) sample was the most interesting, showing good drying up to the maximum 250 ft/min test speed.

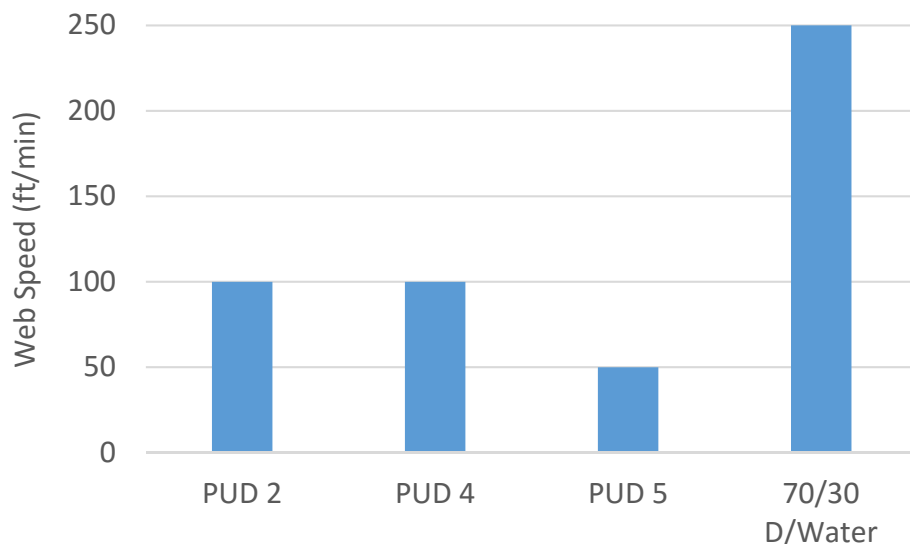


Figure 11. Maximum web speed for dry, tack-free cure with 40 kGy EB dose.

Conclusions

The results of this study show that water based acrylate functional materials including water soluble monomers and PUDs can be effectively EB cured. For some materials high conversions can be achieved at relatively low dose levels. One of the most interesting aspects of the results was that good curing was achieved in a single EB curing step without prior thermal evaporation of water. This could be a unique process advantage for EB; although, a direct comparison to UV curing was not part of this study.

One potential explanation for the ability to dry and cure in one step could be the nature of the EB curing process itself. EB provides uniform energy deposition throughout the thickness of the coating layer. This is in contrast to UV where the energy is most concentrated at the surface.⁶ Given this EB curing process, it is possible water may be driven to the surface by the curing and crosslinking of the polymer layer. This could also be facilitated by heat generated in the exothermic curing process. Water which evaporates from the coating surface would be expected to be rapidly purged from the EB reaction chamber by the dry nitrogen that is used for inerting.

The ability to EB dry and cure water based materials in one step could have practical implications for a number of commercial applications. These could include:

- Ultra-low migration coatings for food packaging that do not contain low molecular weight monomers
- Low migration inkjet inks with low viscosities for jetting enabled by using water as a diluent
- High performance industrial coatings with physical properties enabled by the use of higher molecular weight materials dispersed in water.

Another advantage of EB curing of water based materials is curing in the absence of photoinitiators. While a large number of photoinitiators are available for UV curing, some can be challenging to use in water based formulations. Some photoinitiators may be difficult to solubilize or disperse in water. Also, the initiator may interfere with the stability of the reactive polymer emulsion or dispersion. The absence of photoinitiator further enhances the ability to develop low migration materials.

EB energy can penetrate opaque materials without concern for optical density. This allows curing of highly pigmented or filled coating layers. This feature may be enhanced when water is used for viscosity reduction allowing the application of coatings with very high levels of pigments or fillers.

References

1. C. Decker and I. Lorinczova, "UV-Radiation Curing of Waterborne Acrylate Coatings", *Journal of Coatings Technology Research*, Vol. 1, No. 4, p. 247 (2004).
2. R. Awad, and F. Lunger, "New Developments in Waterborne UV Resins for Wood Coating", *RadTech Europe Conference Proceedings 2001*, p. 415.
3. S. Chatterjee, M. Laksin, D. Biro, J. D. Turgis, "Radiation Curable Aqueous Composition", US Patent 7,037,953, May 2, 2006.
4. M. Laksin, S. Chatterjee, V. Linzer, "Method and Apparatus for Wet Trapping with Energy-Curable Flexographic Liquid Inks", US Patent 6,77,683, August 10, 2004.
5. M. Laksin, S. Evans, K. Fontaine, S. Chatterjee, "EB Gravure – Novel printing Concept for Sustainable Packaging", *RadTech North America Conference Proceedings 2010*.
6. S. Lapin, "Comparison of UV and EB Technology for Printing Packaging Applications", *RadTech Report*, September/October 2008, p. 27.

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