Adhesion Promoters for EB Cure

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Abstract

Several common methods for improvement of adhesion for EB cured systems have been reviewed. Four carboxylic acid functional acrylates were evaluated as adhesion promoters for use in EB cured coatings and laminating adhesives. The cycloaliphatic acid functional acrylate demonstrated improved and more consistent adhesion than the aliphatic and aromatic backbone based acrylates. These acid functional acrylates demonstrated good adhesion in EB cured laminated structures with some of the adhesion trends from the testing of these structures applicable to the performance in the EB cured coatings.

Introduction

Formulation of EB cured coatings with good adhesion to plastic substrates remains one of the most challenging tasks for formulators[1]. Most of the EB cured coatings are designed to meet specific properties that are often achieved at the expense of adhesion. For example, scratch resistant high gloss finishes are obtained using multifunctional acrylates, which when cured, cause the coating to undergo a significant degree of shrinking leading to a loss of adhesion. Slip aids used to achieve the necessary coefficient of friction can also interfere with adhesion. In order to reduce the skin irritation and odor when dealing with the liquid formulations, alkoxylated acrylates are selected and these often have worse adhesion to plastic substrates than the non alkoxylated monomers. Following a drive to reduce packaging costs, a wide variety of relatively inexpensive unprimed plastic substrates has recently become available, which makes adhesion of energy cured coatings and adhesives even more relevant and important. In this paper, we discuss the most common approaches to solving adhesion issues for EB cured laminating adhesives and coatings. We also demonstrate the utility of acid functional adhesion promoters for use in EB cured systems.

Common Methods to Improve Adhesion for Energy Curable Formulations

Several methods are commonly used to improve the adhesion of the EB curable formulations:

- Substrate surface modification by mechanical means or via corona treatment,
- Application of a primer that is typically either a solvent or water borne,
- Use of wetting additives that do not interfere with adhesion (typically perfluorinated or non silicon based surfactants, or low surface tension acrylate monomers),
- Coupling agents & dual cure systems,
- Selection of acrylates with reduced shrinkage, good adhesion and formulating to impart flexibility to the coatings,
- Use of adhesion promoters.

Very often these methods are used in combination. The inline corona treatment is typically a part of coating/printing processes on flexible plastic substrates due to the ease of installation of the equipment and relatively low cost of operation. While corona treatment is intended for uncoated films, primed films can also be treated to further improve wetting and adhesion.

Formulators typically select acrylates with good adhesion to the substrate, low shrinkage and sufficient reactivity to meet the coating performance requirements. Various adhesion promoters are often used as part of formulations to either improve or impart adhesion to the substrate.

Silane coupling agents[2] have been historically used to improve adhesion of various polymers to various inorganic substrates including glass. These molecules usually possess at least two key functional groups: one to bond with the polymer and another to bind to the substrate surface via a non energy cure pathway. They were later used to create the so called "dual cure" systems, where the primary UV/EB photopolymerization was accompanied by the secondary "dark cure" stage, which could be a moisture or heat driven reaction with the functional groups on the substrate. Common examples are trialkoxysilylamines- these are incorporated into the coating by reacting the amine groups with epoxy, acrylate or isocyanate functional groups, thus creating various dual curable systems[3]. Dual or hybrid energy curable coatings based on the combination of the energy cure and moisture cure of isocyanate groups are also well known[4] as are reactive primers such as polyethyleneimines, which improve adhesion of coatings to various substrates[5].

## Utility of Non Reactive Polymeric Adhesion Promoters
Addition of reactive moieties into energy curable coatings may render the formulations more sensitive to moisture and make them less stable at elevated temperature. The majority of currently used adhesion promoters are non reactive materials that can be separated into two groups of compounds:

- Non reactive adhesion promoting resins in acrylate monomers
- Acid functional acrylates

The non reactive adhesion promoting resins are typically low to medium molecular weight polymers chosen based on their ability to adhere to a specific substrate. Among these are polyacrylates with or without the acid functional groups, chlorinated polyolefins, various rubbers, polyesters, polyols and various copolymers chosen for their adhesion to a variety of plastic films.

The non reactive polymer based adhesion promoters often impart adhesion to energy curable coatings in several ways. First, they themselves have excellent adhesion to the substrate. Secondly, the large non reactive, linear or branched polymer molecules reduce the shrinkage of the crosslinked coatings, which in turn, reduces the stress created at the coating-substrate interface, leading to improved adhesion. Third, they can impart toughness, flexibility and even elasticity to the coating, which would further improve the adhesion, especially for flexible substrates.

The adhesion promoters based on the "adhesion polymers" also face a major challenge: they have to be easy to process and compatible with the other components of the coatings. Most of these resins are solid and have to be dissolved or dispersed in a suitable monomer prior to addition to the formulations. Unfortunately, most of the monomers that readily dissolve these resins are, either high Draize materials such as 1,6-hexanediol diacrylate (HDODA) and trimethylolpropane triacrylate or are high odor materials like phenoxyethyl acrylate and isobornyl acrylate. However, a *claimed* benefit of using these monomers is their ability to penetrate and swell some plastic substrates and form semi-interpenetration polymer network after cure and thus improve adhesion. Scheme 1.

Non-reactive adhesion promoter

Plastic substrate

Semi-IPN formed by substrate
and swelled and then UV cured monomer
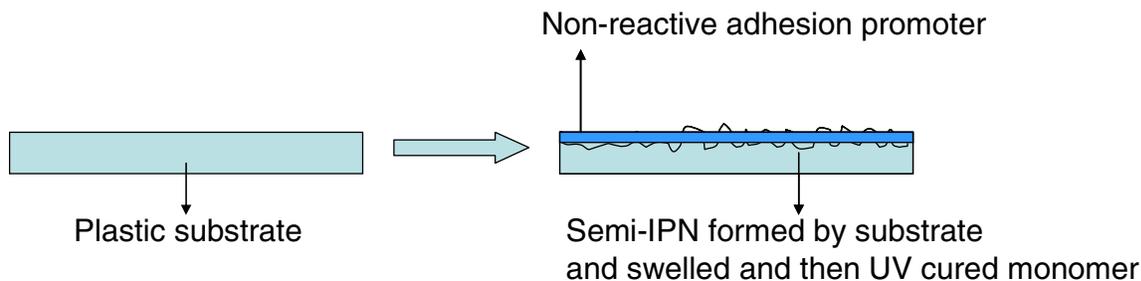
Scheme 1. Pictorial representation of a cross section of a plastic substrate swelled by a UV monomer and bonding to a non-reactive adhesion promoting linear polymer.

Challenges for the Acid Functional Adhesion Promoters

The acid functional acrylate adhesion promoters typically improve the adhesion due the presence of the polar acid functional groups. These are most commonly carboxylic acid groups and less commonly sulfonic and phosphonic acid groups. Over the years a variety of different acid functional acrylates have been used to enhance the adhesion of energy curable systems[6a,b,c]. They vary in their effectiveness and are all plagued by the same major disadvantage: incompatibility with tertiary amines, which are used to accelerate the UV cured systems. Fortunately, EB coatings are cured under nitrogen and do not require amine synergists, thus making acid functional adhesion promoters a more relevant option.

The major issue with both types of the adhesion promoters is that they often do not create sufficient adhesion. This can be linked to several problems:

- Raw material suppliers position adhesion promoters as "additives"
- Difficulties in testing adhesion of EB cured coatings
- Adhesion promoters designed for use in adhesives are often used in coatings

The term "adhesion promoter" typically leads to an erroneous assumption that these are non critical, coating "aids" that are supposed to improve adhesion for any coating system when used at the low "additives" levels- typically no higher than 5%. Unfortunately, it has been the author's experience that due to the multitude of different coating requirements, curing conditions and substrates the additive level approach has not been successful. This is in large part because adhesion promoters are added to formulations as an afterthought often resulting in only partial improvement in adhesion and affecting other coating properties such as hardness, scratch and solvent resistance. The cause for the adhesion failure is seldom established-typically the adhesion promoter is blamed for the ineffectiveness rather than the design of the entire coating system.

The other part of the problem comes from the way the adhesion is tested. While there are effective test methods to test for adhesion, most of these were designed for testing adhesives[7] and difficulties arise when converting these tests to testing adhesion for coatings. Two of the most common tests for adhesion for energy curable coatings are the tape tests and the crinkle test that is often used for flexible substrates.

In the tape test[8], the coating is cut with a thin blade and a pressure sensitive tape is applied to the cross cut area, which is then removed. The adhesion is considered to be acceptable if no coating has been removed with the tape. Because a grid is often cut on the coating-the amount of coating remaining on the substrate after the peel can be quantified (either as % area remaining or number of cells remaining) and used to judge whether the adhesion is improving in the test sequence. Despite the potential for inconsistent results, this test is widely accepted by formulators and converters and leads to satisfactory results, though either an agreement of all parties on the specifics of the test is needed or a good correlation is needed between the test details and the actual coating performance.

The crinkle test exists in several modifications where the coated film is "crinkled" by hand typically at ambient temperature[9]. The coating is then either peeled by a pressure sensitive tape or visually inspected for damage. The test looks at both, the adhesion and the flexibility of the coating. This test is useful for the thin film substrates where cutting the coated layer is too difficult without cutting through the underlying film.

Carboxylic Acid Functional Acrylates as Adhesion Promoters

Adhesion promoters are typically molecules that have shown good performance in adhesives. Adhesives and coatings formulations are different and are designed to perform under different stresses, which are reflected in the differences between the test methods. In order to better understand the applicability of the adhesives performance data to the design of coatings with improved adhesion, several acid functional acrylates (also known as acid functional adhesion promoters) have been selected (Table 1). These compounds contain one acrylate or methacrylate functional group tethered to the carboxylic acid functional group via the aliphatic, aromatic or cycloaliphatic backbones.

Table 1. Acid Functional Adhesion Promoters
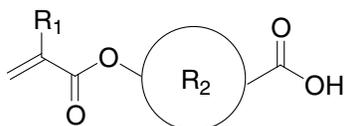
Adhesion Promoter #	R_2	R_1	Viscosity @ 25°C, mPa*s	Tg, °C
AP 1	Aliphatic	H	195	6.5
AP 2	Aromatic	H	3200	44
AP 3	Cycloaliphatic	H	7450	56
AP 4	Aromatic	Me	3763	-

Performance in EB Cured Laminated Structures

The acid functional acrylates were first tested as EB cured homopolymers bonding two selected substrates. The laminated structures were cut into 1 inch wide strips and peeled at 30 cm/min using Thwing-Albert peel tester, and the results are summarized in Table 2.

Table 2. Peel Strength for the EB Cured Laminates[*]

Substrates[**]	AP 1	AP 2	AP 3	AP 4
BOPP to BOPP	118	42	595 SF[***]	709 SF
PET to PET	381 SF	618 SF	805 SF	21
PET Barrier to self	31	21	24	11
Metallized BOPP to BOPP	22	129	45	16

*AEB lab unit, 30 KGy, 100 kV, 5mA, 50 fpm, <200ppm O_2, coated to 0.3mil (7.6μm) thickness
**BOPP film: AET #T523, 100 gauge (25 μm), both sides treated, surface energy 34-36 mN/m
   PET film: DuPont Teijin Films Mylar 48 LBT, inside corona treated, surface energy 34-36 mN/m
   PET Barrier film: DuPont Mylar Barrier film M34 50 LBT, PVDC coated inside, surface energy 36-38 mN/m
   Metallized BOPP: AET MT 70 gauge film (18 μm), outside treated, surface energy 30-32 mN/m, laminated to the BOPP film
***180° peel values in g/inch. Peak value with substrate failure (SF), otherwise a kinetic mean bond values for the peel strength are reported

As can be seen from Table 2, there was a difference in bond strength between the adhesion promoters and between the substrates. All four acid functional acrylates formed EB cured homopolymers with high bond values to at least one film type. Thus, AP1 and AP2 formed good bonds with corona treated PET but not with primed BOPP, AP4 formed strong bonds only with BOPP film while AP3 formed good bonds with both, BOPP and PET films. Neither acid functional acrylate formed strong bonds with the PVDC coating and with metallized film.

Based on these results, we can assume that AP3 and AP4 might work best as adhesion promoters for EB cured coatings on treated BOPP films, while AP1, AP2 and AP3 could work for adhesion to corona treated polyester films. None of the acid functional acrylates are expected to perform well as adhesion promoters for the PVDC barrier coated film or for metallized films.

Performance in UV Cured Laminated Structures

As can be seen from Table 3, similar conclusions[10] can also be made from the UV cure results for the laminates. Laminated structures containing each of the acid functional acrylates were cured in the presence of a photoinitiator (Irgacure 819 at 3 wt%). AP3 and AP4 demonstrated high bond values with BOPP. Laminates with AP1, AP2 and AP3 resulted in film destruction on PET while no adhesion promoter had good adhesion to the metallized film.

Table 3. Peel Strength for the UV Cured Laminates[*]

Substrates	AP 1	AP 2	AP 3	AP 4
BOPP to BOPP	145	29	670 SF	778 SF
PET to PET	591 SF[**]	642 SF	701 SF	1
PET Barrier to self	23	6	10	18
Metallized BOPP to BOPP	9	22	50	7

* Lesco UV lab unit, H-bulb, 100mJ/cm², 695 mW/cm², 120fpm, coated to 0.3mil (7.6μm) thickness
**180° peel values in g/inch; peak value with substrate failure, otherwise kinetic bond values are reported

Though some differences will exist, the trends for adhesion appear to be similar for the UV and EB cured laminated systems since both were cured under inert conditions. Additional complexity of the UV cured systems due to the presence of the larger number of variables (i.e. exposure levels, initiators

used, atmosphere vs. inert cure, light absorbance by substrates, etc.) makes it less practical to attempt to translate results from UV cure to EB cured systems and vice versa.

Acid Functional Acrylates: Homopolymers vs. Copolymers

The homopolymers obtained by EB cure of the acid functional acrylates were shown to have varied adhesion to the selected substrates. Since these acrylates are available in a relatively wide viscosity range from ca. 200 to ca. 7500 mPa∗s, their blending may be used to adjust viscosity of the formulation. However, as can be seen from Table 4, the addition of the lower viscosity aliphatic acid functional acrylate AP1 reduced the bond strength of AP2, AP3 and AP4, though at lower 25% level the bond values were still sufficiently high to cause substrate destruction during the peel test. Blending AP1 and AP2 did not improve their weak bonds on the treated BOPP film. However, blending AP2 with AP3 and AP4 resulted in high bond values that were typical of AP3 and AP4 on BOPP film. The results could be due to the structural and polarity differences between the linear aliphatic and bulkier cycloaliphatic and aromatic backbones of the acid functional acrylates.

Table 4. Peel Strength for the EB Cured Blends of Acid Functional Acrylates

AP 1, %	25		50			50	50	
AP 2, %	25	33	50	50				50
AP 3, %	25	34		50	50		50	
AP 4, %	25	33			50	50		50
Peel Strength	**410 SF**	**831 SF**	**43**	**434 SF**	**558 SF**	**246**	**55**	**834 SF**

 *BOPP to BOPP, AEB EB lab unit, 30KGy, 100kV, 5mA, 50 fpm, <200ppm O_2, coated to 0.3mil (7.6μm) thickness
**180° Peel values in g/inch, peak values with substrate failure, otherwise kinetic bond values are reported

The viscosity reduction as well as other property modifications can be achieved via addition of other, non-acid functional acrylates. As can be seen in Table 5, addition of some commonly used "adhesion" monomers can reduce the performance of the acid functional adhesion promoters. For example, addition of 1,6-hexanediol diacrylate (HDODA) and 2-phenoxyethyl acrylate (PEA) to the acid functional acrylates AP2 and AP3 resulted in very low bond values in the laminates. At the same time, addition of isodecyl acrylate (IDA) and nonylphenol [4EO]-acrylate (NP[4EO]A) resulted in high bond values with substrate failure-similar to those of the acid functional acrylates themselves.

The improved peel strength in formulations containing a combination of an adhesion promoting monomer IDA and (NP[4EO]A) can be attributed to two factors. The nonyl and isodecyl moieties help reduce the Tg and flexibilize the overall formulation. The surfactant like structure of nonylphenol alkoxylates and IDA helps in reducing surface tension of the formulation, improves wetting and flow out on the substrate, and reduces shrinkage of the cured laminating adhesive.[6b,c]

Table 5. Effect of Non Acidic Acrylates on Peel Values in EB Cured[*] Laminated Structures

AP 3, %	100					50	50	50	50
HDODA, %		100				50			
PEA, %			100				50		
IDA, %				100				50	
NP[4EO]A, %					100				50
Peel Strength,	**595 SF****	**30**	**15**	**8**	**21**	**32**	**54**	**479 SF**	**534 SF**

* BOPP to BOPP, AEB EB lab unit, 30KGy, 100kV, 5mA, 50 fpm, <200ppm O_2, coated to 0.3mil (7.6μm) thickness

Acid Functional Acrylates as EB Cured Coatings on Plastic Substrates

Despite the multiple differences between laminating adhesives and coatings, the question remains whether the information obtained by testing of the laminated structures can be used to select adhesion promoters for use in EB cured coatings. Table 6 contains results from testing EB cured acid functional acrylates as coatings on several film substrates at the same coating thickness. Since very low adhesion values were obtained for the PVDC film-it was not used for the coatings tests.

Table 6. Adhesion Tape Test* Results for EB Cured Coatings**

Substrates***	AP 1	AP 2	AP 3	AP 4
BOPP	0	cohesive failure	100%	100%
PET	0	partial adhesion	100%	cohesive failure
Metallized BOPP	100%	0	0	0

*Crosshatch test with 3M 810 Tape. 0 is complete film removal from substrate, 100% means no film removal from the substrate, cohesive failure=coating evenly split between tape and substrate, partial adhesion = partial coating removal from substrate
**AEB EB lab unit, 30KGy, 100kV, 5mA, 50 fpm, <200ppm O_2, coated to 0.3mil (7.6µm) thickness
***BOPP film: AET #T523, 100 gauge (25 micron), both sides treated, coated on the inside
   PET film: DuPont Teijin Films Mylar 48 LBT, coated on the corona treated side
   Metallized BOPP: AET MT 70 gauge film (18 micron), outside treated, coated on the metallized side

Once EB cured, AP1 and AP4 formed tacky coatings while AP2 and AP3 formed dry to touch films. Tacky coating surface would present problems for the testing since there would be additional bonding to the peeling tape that should not be present in the coatings with typically non tacky, well cross linked surface. AP1 showed no adhesion in the test with the 3M 810 tape on BOPP while AP4 showed excellent adhesion to the BOPP substrate. However, AP1, the most polar adhesion promoter showed very good adhesion to the metallized film when applied as a coating, even as no adhesion was seen in the laminated structure. AP2 demonstrated a cohesive failure on BOPP, where the coating was evenly split between the tape and the substrate. AP3 showed similar excellent adhesion to the BOPP film as was seen in the laminated structures. On PET substrate, AP1 was also completely removed from the film surface with the tape while AP4 had cohesive failure. AP2 was partially removed from the PET film while AP3 showed very good adhesion to the substrate with no coating removed by the testing tape.

Thus, the results from the testing of the homopolymers of the EB cured adhesion promoters for adhesion in laminated structures did not have a simple correlation with the results for the adhesion as a coating to a single substrate. Although, among the acid functional acrylates tested, AP3 showed good adhesion in both, the laminated structures and on the single substrate. Based on these results we rank the acid functional acrylates in the order of increasing overall performance for adhesion as follows:

$$AP\ 1 \leq AP\ 2 < AP\ 4 < AP\ 3$$

The above ranking of the adhesion promoters was done based on their performance in laminated structures and as coatings on single substrates at a specified coating and substrate thicknesses. However, it is unclear whether this ranking would also apply to a broader selection of substrates and coating thicknesses. To address this concern, the homopolymers of the adhesion promoters were also tested at a higher coating thickness on several flexible and rigid substrates. This time the tape test was done with two 3M 810 and 610 tapes and the results were similar (Table 7).

As can be seen from Table 7, AP3 still had very good adhesion to treated BOPP film, PMMA sheet and PC film but had no adhesion to the corona treated thicker PET film. Only AP4 was found to have adhesion to PET film, though it had no adhesion to the polycarbonate film. AP2 had adhesion only to BOPP film while AP1 had no adhesion to any of the substrates. Based on these results, for thicker coatings, we rank the performance of the adhesion promoters slightly differently as follows:

$$AP1 < AP2 << AP\ 3 \approx AP\ 4$$

Table 7. EB Cured* Coatings on Plastic Substrates: Adhesion Tape Test**

Substrate***	AP 1	AP 2	AP 3	AP 4
BOPP	0	5	5	5
PET	0	0	0	5
PMMA	0	0	5	5
PC	0	0	5	0

* AEB EB lab unit, 30KGy, 100kV, 5mA, 50 fpm, <200ppm O_2, coated to 0.5mil (12.7μm) thickness
** Crosshatch tape test; ranked from 0 to 5, where 5 is no coating detached, 0 is complete coating detachment.
*** BOPP = 2mil BOPP film, coated on corona treated side, surface energy 32-34 mN/m
    PET = Tairilin BH-116 clear, 188μm PET film, coated on corona treated side, surface energy 38 mN/m
    PMMA = Acrylite FF sheet, 0.177 inch gauge, untreated, surface energy 38-40 mN/m
    PC = Sabic 10mil polycarbonate film, surface energy 36 mN/m

Acid Functional Acrylates in EB Cured Coating Formulations

The homopolymers obtained by EB cure of the selected acid functional acrylates possess the ability to form strong bonds in laminated structures and demonstrate good adhesion to some substrates as coatings. However, it is not yet clear whether these compounds could be used to improve adhesion of formulated EB cured coatings where other acrylates and performance enhancing additives are present. To determine this, we tested the acid functional acrylates in a coating formulation containing a commonly used low viscosity (400 mPa*s @ 25°C) tetrafunctional polyester acrylate oligomer and a trifunctional monomer trimethylolpropane[3EO] triacrylate (TMP[3EO]TA). To improve the wetting of the films without reducing adhesion, a polyacrylic surfactant from Cognis was chosen. The coatings were EB cured on the treated BOPP film and tested for adhesion and hardness (Table 8).

Table 8. Adhesion for EB Cured* Coatings on BOPP Film

Polyester Acrylate, %	44	32.9	32.9	32.9	32.9
TMP[3EO]TA, %	55	41.1	41.1	41.1	41.1
AP 1, %		25.0			
AP 2, %			25.0		
AP 3, %				25.0	
AP 4, %					25.0
Wetting Agent, %	1	1	1	1	1
Tape Adhesion**	**0**	**0**	**1**	**3**	**0**
Pendulum Hardness***	254	263	254	293	88

* AEB EB lab unit, 30KGy, 100kV, 5mA, 50 fpm, <200ppm O_2, coated to 0.5mil (12.7μm) thickness
**Crosshatch tape test using 3M 810 tape; ranked from 0 to 5, where 5 is no coating detached, 4 less than 5% of coating area flaked, 3 coating detached from 5-15% of area, 2 coating detached from 15-35% area, 1 coating detached from 35-65% area, 0 is complete coating detachment.
***Measured for the coatings on glass

As can be seen from Table 8, at 25 wt% level, two of the four acid functional acrylates improved coating adhesion over the original system, where AP 3 had improved the adhesion the most, followed by AP 2, while AP1 and AP4 had no measurable contribution. The hardness of the coating was measured and was found to be only slightly modified by the presence of AP1 and AP2, increased with AP3 and significantly decreased for AP4. Data in Table 8 shows that it is possible to formulate EB coatings with improved adhesion without compromising the coating hardness.

A higher level of addition of an acid functional acrylate can further improve the adhesion (Table 9). When used in a similar system as above with the same tetrafunctional polyester acrylate and glycerol propoxylated (3PO) triacrylate (GPTA) the adhesion increased with the increasing levels of the adhesion promoter. These results suggest that in order to obtain sufficient adhesion to a substrate, a higher than the additive level of an acid functional acrylate may be needed, potentially making the adhesion promoter a significant component of the formulation.

Table 9. Effect of Acid Functional Acrylate Level on Adhesion on BOPP Film

Components	A	B	C	D
Polyester Acrylate, %	44.03	37.36	30.70	24.02
GPTA, %	55.03	46.70	38.36	30.04
AP 3, %	0	15.00	30.00	45.00
Wetting Agent, %	0.94	0.94	0.94	0.94
Tape Adhesion**	**0**	**1**	**2**	**5**

* AEB EB lab unit, 30KGy, 100kV, 5mA, 50 fpm, <200ppm O_2 coated to 0.5mil (12.7μm) thickness on BOPP
**Crosshatch tape test using 3M 810 tape; ranked from 0 to 5, where 5 is no coating detached, 4 less than 5% of coating area flaked, 3 coating detached from 5-15% of area, 2 coating detached from 15-35% area, 1 coating detached from 35-65% area, 0 is complete coating detachment.

Conclusions

Acid functional acrylates can be considered viable adhesion promoters for EB cured applications. The homopolymers of EB cured acid functional acrylates possess adhesion to various plastic substrates in laminated structures and as coatings. The acid functional acrylates can also improve adhesion in formulated EB cured coatings, though at much higher than "additive" levels. Cycloaliphatic acid functional adhesion promoters impart improved adhesion over aliphatic and aromatic backbones, though blends of acid functional acrylates with different backbones can also be used. While some adhesion trends can be transferred from the tests with laminated structures to coated structures, sufficient differences exist to limit this approach in selection of adhesion promoters for EB cured coatings.

References:
1. A. Carroy et al., "How to Get Enhanced Adhesion to Plastic Substrates", Radtech Europe 2005.

2. E.P. Plueddemann: "Silane Coupling Agents", Plenum Press, 1991.

3. See for example: K. Gaglani, "Dual Curing Conformal Coatings", US 5,312,943.

4. E. Skinner et.al. "Interpenetrating Dual Cure Resin Compositions", US 4,342,793. Also, see: T. Iimure, US 4,961,960 and references cited therein.

5. S. Rice et.a. "Polymeric Film Coated In-Line with Polyethyleneimine", US 5,156,904. Also, see: Pang-Chia Lu et.al. US 5,776,604

6. a) For example: K. Rea et.al. "Radiation-Cured Laminated Flexible Packaging Material", US 6,908,665; US 6,472,056.
b) Ramesh Narayan and Ning Chen, Cognis Corporation, Radtech 2000, "Energy curable pressure sensitive adhesives: Recent developments"
c) Ramesh Narayan, Ulrike Varlemann, Ning Chen and Arifin Marzuki, US 7,385078 (2008) to Cognis Corporation

7. For peel tests of adhesive bonds see: ASTM D903, D1876. For a lap shear test refer to ASTM D1002. For tack measurements of adhesives see: ASTM D2979, D3121. Adhesion of a PSA tape to paperboard can be done by ASTM D2860. The 180° peel test for pressure sensitive tapes is described under ASTM D3330. The torque strength of adhesive joints between rigid substrates can be measured by ASTM D3658.

8. Standard Test Method for Measuring Adhesion by Tape: ASTM D 3359.

9. Ice water crinkle test is typically used for testing adhesion for inks and laminated systems.

10. The double bond conversion was similar in this case between the UV and EB cure, since in both cases the cure was under inert atmosphere. As measured by FTIR (monitoring the peak at 812 cm^{-1}), for AP3 EB cure led to 78.4% double bond conversion while UV cure led to 77.1%.