UV curable laminating adhesives

Dr. Jeremy Yatvin

allnex Alpharetta, USA

May 2022

Laminating adhesives are unseen features of modern everyday life for a host of consumer goods. Nearly any product with plastic packaging integrates a laminating adhesive to create additive properties of the films. It is difficult for a single extruded film layer to incorporate printability, water barrier, air barrier, elasticity, glossiness, or a host of other desirable chemical properties on its own. A plastic good consisting of multi-layer packaging incorporates adhesives to obtain a final film with several simultaneously desired properties.[1] To attach these layers requires adhesives with good adhesion to two often completely different polymers, such as polydivinylidene chloride and PET. And if there are three or more layers, as is common, an adhesive between each layer is usually chosen to be interface specific.

These adhesives can come from all of the most common coatings chemistries such as polyacrylics, two-part urethanes, cyanoacrylates and more. However UV curable laminating adhesives offer the unique benefits of UV chemistry with extremely fast cure times, high throughput, low VOCs, and long pot lives.[2]

An important factor to consider when choosing a UV curable laminating adhesive is the substrate's light absorbing properties, since the user must irradiate through the plastic film. At least one side of the substrate must be transparent to the output of the user's lamp. PET, for instance, has poorer transparency to Hg lamps that emphasize shorter wavelength output than to longer wavelength LED sources.

A good adhesive must, of course, generate strong bonding properties with the substrate. This is often attained through polar interactions, hydrogen bonding, and van der Waal forces. These are typically considered "weak" bonding forces in comparison to covalent or ionic bonds. Often polymeric substrates that are very hydrophobic and inert, such as PET or polypropylene, are corona or flame treated to generate -OH and -COOH functional groups for resins to interact with.[3] In this work we look at a 4 acrylate functional reactive polyester resin (RPR) that can form ionic bonds with these -OH and COOH groups and boost the adhesive properties of UV-curable laminating adhesives. We also look at the interplay of using varying functionalities of urethane acrylates (UA), conversion, and how those changes affect adhesion.

Experimental procedure

A mixture of acrylated resins with 2% w/w TPO-L are spread between two pieces of 0.5 mil Melinex 454 (corona treated PET) and the substrates pressed together. A #0 rod is pressed down on top and slowly rolled down to evenly spread resin between substrates to give a ~3 um film measured by micrometer screw gauge. The sample is then passed under a Phoseon

Technology FireJet FJ200 16W 395 nm LED lamp at the desired speed and lamp output at a distance of 2 cm.

The cured sample is cut into 1 in wide strips for T-peel test ASTM D1876 for peel separation strength of two flexible materials. These samples are clamped in place and tested on an Instron 5900R to obtain an adhesive strength in Newtons. The noisy initial force spike is ignored and the steady state force value is recorded. 3-5 strips were measured per experimental datapoint. All failures were recorded as adhesive failures.

To measure double bond conversion, a Thermo Scientific Nicolet 6700 FTIR with a diamond single reflection ATR attachment was used. A split open cured sample was screwed down against the window and the urethane peak at 770 cm^{-1} and alkene peak at 810 cm^{-1} were integrated. The same peaks were measured on a drop of uncured resin, and by taking the comparative ratios, alkene conversion can be determined.

Results and discussion

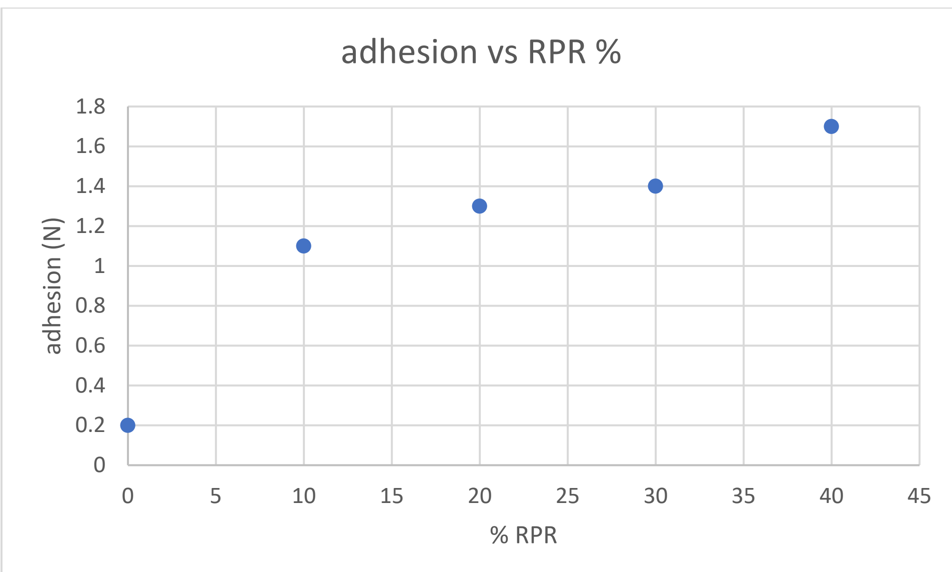

Figure 1 adhesion versus % RPR

	A	B	C	D	E
PPTTA	49	38	28	18	8
RPR	0	10	20	30	40
UA-6f	49	50	50	50	50
TPO-L	2	2	2	2	2
sum	100	100	100	100	100
adhesion (N)	0.2	1.1	1.3	1.4	1.7
conversion %	58%	74%	73%	74%	72%

Table 1 Formulas and evaluation of % RPR

Pentaerythritol (5 EO) tetraacrylate (PPTTA) was used as the reactive diluent of choice throughout the experiments. We see that the inclusion of even 10% RPR strongly improves adhesion in a 600 mJ/cm^2 irradiated film (Figure and table 1), and further increases in concentration continue to boost adhesion, albeit to a lesser degree. We see that alkene conversion stalls at around 72%, an interesting phenomenon considering that oxygen inhibition is minimal in a film sandwiched system.

It is apparent from this data that the RPR is reacting with surface -OH and -COOH groups as desired, and increasing the adhesion by 500+%. This surface reaction is fast, as we do not see much change in adhesive properties with time due to further reaction or relaxation of the polymer network. A 2f UA with 25% RPR was cured and examined at 1 hour, 24 hours, and 3 months (not shown) and no significant difference in adhesion was observed.

Formulation D above was irradiated at several different energy densities by adjusting the lamp output (Figure 2). We observe that both adhesion and conversion increase with higher irradiation, but a maximum is reached by 150-200 mJ/cm^2, a quite low dosage. Double bond conversion also tops out at the same point as adhesion.

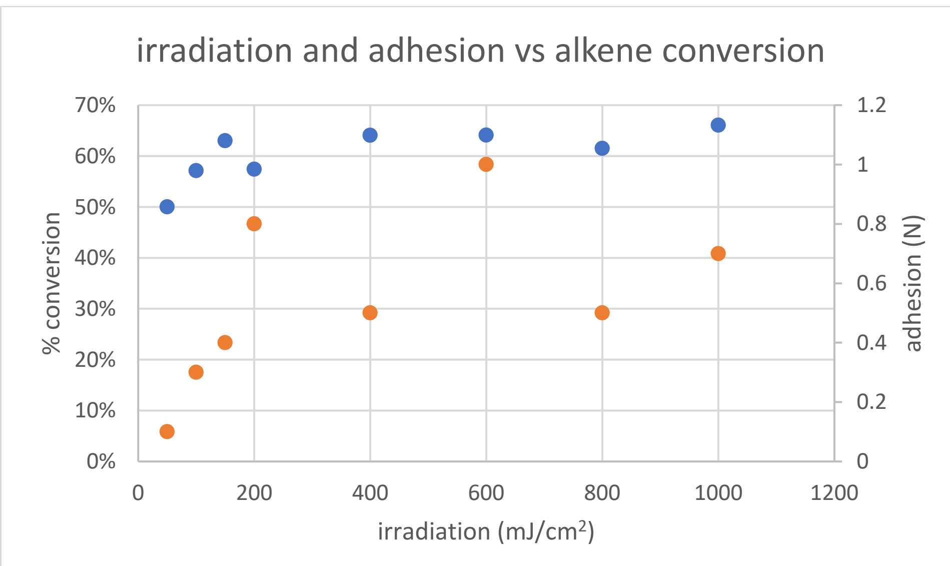

Figure 2 percent conversion and adhesion vs irradiation

The laminate ceases free radical polymerization at 65-70% double bond conversion due to the system quickly reaching too high viscosity for diffusion. Nearly a third of the double bonds remain for reaction, but they are bound in matrix and unable to be reached by propagating radicals. Even repeated passes under the lamp does not increase alkene conversion. It is curious to note that the difference between minimal adhesion and a well performing adhesive is as little as 10-15% alkene conversion, showing how tight the formulation window can be.

An adhesive needs to retain a measure of elasticity, and very densely crosslinked materials are known to be brittle and have minimal flexibility. By finding the “sweet spot” of crosslink density to give strength without inducing brittleness, we can maximize the qualities of the adhesive. RPR is a higher (4) functional material whose inherent mechanical properties are not very good, so using it in very high proportions in the formulation is not necessarily the best option. However urethane acrylates are well known for having superior mechanical properties, and are available with several different functionalities. By comparing a cross section of materials, we can observe what functionality serves best.

	A	B	C	D	E	F
PPTTA	19	19	19	19	19	49
RPR	29	29	29	29	29	
UA-2f	50					
UA-3.5f		50				
UA-4f			50			
UA-6f				50		49
UA-10f					50	
TPO-L	2	2	2	2	2	2
sum	100	100	100	100	100	100
% conv	91%	92%	94%	76%	64%	58%
adhesion (N)	0.3	0.2	0.3	0.8	0.5	0.4

Table 2 UA formulations with conversion and adhesion

We see from this chart that conversion and brittleness are very crucial aspects of a good UV laminating adhesive (Table 2). A 50% of UA-2f (2 functional), UA 3.5f, or UA-4f leads to high (>90%) conversion (sample A,B,C), and despite the 30% RPR content, they are roughly equivalent to an adhesive without an RPR (sample F). The trend overall is that higher functionality UAs give better adhesion, and at least part of this behavior may be attributed to their ability to quickly gel a system at lower conversion. The resulting film is less brittle, probably due to the plasticizing nature of the unreacted pendant acrylate groups. However, extremely high functional UA-10f (E) caused gelling so early in the reaction (64%), that the material was not able to reach as high strength as UA-6f (D).

Conclusion

RPR is a powerful new resin technology for promoting adhesion to -OH and -COOH functional substrates. This work studied corona treated PET due to its known challenging nature, but we also have seen high effectiveness on various treated BOPPs and untreated PLA. However, surface adhesion is not all there is to preparing a good adhesive. A material that balances toughness with elasticity is also important. As highlighted here, one method to attain that is though the usage of high functionality urethane acrylates that impart good mechanical properties while to modulating crosslinking conversion and density.

1. J. Goodman; *Multilayer Flexible Packaging*, 2nd Edition. Elsevier, 2016

2. R. Schwam; *UV Coatings: Basics, Recent Developments and New Applications*, 1st Edition. Elsevier, 2007
3. A. Yiaizis et al.; A novel atmospheric plasma system for polymer surface treatment in *Polymer Surface Modification: Relevance to Adhesion*, 2000, vol 2, pp 65-76