A Formulator's Guide To Energy Curable Laminating Adhesives

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Laminating adhesives (LA's) comprise a relevant and growing segment among energy curable product markets. Initially regarded as being too expensive and not technically advanced enough for most laminating applications, energy curable laminating adhesive products have become major players in the converting and packaging industries, particularly in specialty applications. Although still just a small portion of the USD $30 Billion plus world adhesive market, its role as a continually growing market segment has become significant in the overall adhesive picture.

Laminating adhesives are used in food, medical, and industrial packaging. Recently, development work in the realm of food packaging has formed a profitable business base for those willing to implement this technology.

The flexible packaging market has seen rapid growth owing to the unique combinations of energy curable laminating adhesives and substrates available to more effectively packaged products. New forms of flexible packaging like the stand-up pouch are making products easier to use and more attractive to consumers.

Benefits of Energy Curable Laminating Adhesives

Laminating adhesives generally bond clear laminate plastic films to other various plastic films, paper or metallic foil substrates. They may be applied by roll coat, flexographic, blanket or screen processes. Depending on the substrate, whether clear or opaque, curing by UV or electron beam (EB) can offer excellent bond adhesion.

A "dry" type of laminating adhesive offers a non-tacky film that bonds sufficiently to the respective substrates and achieves excellent T-Peel properties when cured. However, when adhesion to a particular substrate is difficult or with opaque substrates, electron beam or PSA-type "wet" laminating adhesives may be necessary.

After cure, a PSA-type of adhesive results in a tacky film which provides a good balance of flexibility, adhesion and cohesion for high peel values, but very rarely will result in substrate failure or tearing of plastic film. PSA-type laminating adhesives can be cured prior to lamination if desired.

Electron beam curing uses high energy electrons to polymerize and crosslink polymeric materials without the use of photoinitiators. This technology reduces curing time and is ideal for opaque substrates due to its penetrating power.

In flexible packaging, UV laminating adhesives have gained popularity in the label industry as an alternative to pressure sensitive labels. Lamination provides protection of printed graphics against abrasion, chemicals, moisture, scuffing and tearing.

UV/EB laminating adhesives offer the ability to laminate at high speeds and at lower drying and total energy costs. Laminated products can be immediately processed since there is instant cure and bond development after energy curing. These adhesives are environmentally friendly, easy to handle, provide excellent lamination, and product shipment is possible within hours after cure instead of days versus traditional water or solvent based laminating adhesives.

Formulating

Our target in this study consisted of formulating applicable Energy Curable laminating adhesives for various uses. For many applications, especially in the packaging industry, in order to compete for volume with conventional adhesives Energy Curable laminating adhesives are formulated from extremely inexpensive products. This helps to make them price competitive in the market. Typically this involves using an inexpensive inert resin, perhaps a hydrocarbon, acrylic, or polyester resin, and adding an inexpensive acrylate monomer and photoinitiator package to create a very low cost Energy Curable laminating adhesive. This type of product will work sufficiently on many substrates, but for higher end specialty applications or more difficult to adhere to substrates, these inexpensive adhesives can fall short of their target in performance. In these cases, a more robust type of laminating adhesive is necessary to achieve successful end properties, which is the type of adhesive that our lab studied during this work.

Being a raw material supplier, our goal was to formulate starting points that our customers could use to become acquainted with our products and the technology and chemistry behind successfully producing Energy Curing laminating adhesives. Unfortunately, previous lab work had illustrated that no single formulation would successfully work in all applications. Every substrate is different, every process is different, and every application's target raw material cost is different. One formulation may be very successful laminating one type of polyethylene to itself, but have extremely poor results when using a different type of polyethylene. This makes formulating these products very difficult, and requires the formulator to have thorough knowledge of Energy Curing technology, substrates, and the laminating process.

The overall goal of most laminating adhesives is to have good adhesion performance, resulting in either substrate failure (tearing of one substrate) or strong adhesive failure (high peel without tearing the substrate). However, depending upon the end application, many other factors may come into play besides good adhesion after laminating. Formulators need to consider such factors as the migration of chemicals, yellowing, reactivity, clarity, temperature stability, and humidity stability in many laminating applications.

There are several types of these more complicated laminating adhesives that have become a major focus in the Energy Curable realm in recent years. Low migration laminating adhesives have been at the forefront of focus in Europe and the United States, while Liquid Optical Clear Adhesives (LOCAs) have dominated the conversation and lab work in Asia. RAHN Group has done substantial work in these areas, but they are not the point of this paper, which will discuss the formulating of non-food grade Energy Curable laminating adhesives for the packaging industry.

Special Products

Of the four Starting Point Formulations that will be discussed here, three of them contain specialty products that help to enhance the adhesive performance of the product. These two products are a

Carboxyfunctional Polyester Acrylate (GENOMER* 7151) and a Phosphoric Acid Adhesion Promoter Additive (GENORAD* 40). As a result of their acidic nature, these products are geared towards exhibiting strong bite into and adhesion on inorganic substrates such as glass and metals. However, they also offer very good adhesion characteristics on certain plastics.

The Carboxyfunctional Polyester Acrylate, GENOMER* 7151, that was formulated with is a monofunctional acrylate with an acid value of 210 mg KOH/g, a Tg of 39ºC, and a viscosity of 7,000 mPas @ 25ºC. This product can be used at high levels in a formulation, but certain existing patents may keep the usage limited. The formulator must investigate such patents before commercializing any adhesive.

The GENORAD* 40 is a methacrylated phosphate ester with an acid value of 340 mg KOH/g, a phosphor content of 11.8%, and a viscosity of 2,000 mPas @ 25ºC. The GENORAD* 40 is generally used as an additive in small doses between 0.5 and 5.0 weight % of a formulation. Being acidic in nature, the use of amines or basic materials can offset any performance gains and possibly cause incompatibility issues when using these products. Fortunately in laminating adhesive applications, amines are generally not needed as there are limited oxygen inhibition problems during the laminating process.

Starting Point Formulations

<u>Low Cost UV Curable LA</u>
<u>SPF 349</u>

Low cost flexo laminating adhesive for treated OPP, PE, PET, and Paper.

Product	**%**
GENOMER* 2252/TM20	38.0
Trimethylolpropane Triacrylate	2.0
Tripropylene Glycol Diacrylate	29.0
GENOMER* 7151	25.0
GENORAD* 40	3.0
GENOCURE* DMHA	3.0
TOTAL	**100**

Properties	
Viscosity (cps or mPa.s @ 25ºC)	850
Reactivity (mJ/cm2)	225

Adhesion Results using T-Peel Test

Substrate Failure results on the following substrate combinations

OPP/OPP	PE/Paper	OPP/Paper	PE/Al Foil
OPP/Met OPP	PET/Paper	PET/Al Foil	PET/PET

Modifications to SPF 349

T-Peel Property

T-Peel properties in "dry" laminating adhesives are dictated by the adhesion of the adhesive to the laminated substrates and by the cohesion of the adhesive. A laminating adhesive with strong cohesion and good adhesion to the respective substrates will offer high T-Peel results.

In SPF 349, the adhesion is supplied by the GENOMER* 7151 and the GENORAD* 40. These products bite into the substrates enough to create a strong adhesive bond. The cohesion is a result of the GENOMER* 2252/TM20 and the Trimethylol Propane Triacrylate, which offer a good amount of crosslink density in the adhesive. This blend of properties resulted in substrate failure for many tested substrate combinations. Increasing these two products will improve the adhesion performance even more.

Reactivity

The reactivity of Energy Curable laminating adhesives is controlled mainly by the amount of functionality formulated into the adhesive, but also by the correct match of photoinitiator to lamp output in terms of energy wavelength.

In SPF 349 using a medium pressure Hg arc lamp at 300 w/cm2, a dose of 225 mJ/cm2 is required for complete cure. This value can vary according to the lamp being used, the output of that particular bulb, and the focus of energy upon the adhesive. Increasing the adhesive's functionality with additional amounts of products like the Trimethylol Propane Triacrylate and greater amounts of GENOMER* 2252/TM20 will tend to increase the system's reactivity. Also a slightly higher amount of GENOCURE* DMHA will tend to increase the reactivity as a greater amount of free radicals will be created to initiate the polymerization process more rapidly. Conversely, adding additional monofunctional products like the GENOMER* 7151 will reduce the reactivity.

Viscosity

The overall viscosity is affected by the inherent viscosities of the raw materials that make up the adhesive. Therefore, low viscosity and low molecular weight products will generally reduce the overall viscosity, while high viscosity and high molecular weight products will tend to increase the system's viscosity.

In SPF 349, additional amounts of the Tripropylene Glycol Diacrylate and the Trimethylol Propane Triacrylate will reduce the viscosity of the adhesive, while the viscosity will be increased with additional GENOMER* 2252/TM20 and GENOMER* 7151.

UV Curable LA for non-PET
SPF 117

Versatile flexo laminating adhesive for treated non-PET film, metallized OPP, AL foil, and Paper.

Product	**%**
GENOMER* 6083/TP	60.0
Dipropylene Glycol Diacrylate	34.0
GENORAD* 40	3.0
GENOCURE* DMHA	3.0

Properties	
Viscosity (cps or mPa.s)	450
Reactivity (mJ/cm2)	100

Adhesion Results using T-Peel Test

Substrate Failure results on the following substrate combinations

OPP/OPP	Met. OPP/PE	PE/PE	PE/Paper

Modifications to SPF 117

T-Peel Property

SPF 117 is an Energy Curable laminating adhesive that consists of inert resin (co-resin) with monomer, photoinitiator and an additive. The major contributor to the T-Peel results comes from the additive, GENORAD* 40. The GENOMER* 6083/TP is another very good contributor to the adhesion of the product. Being an inert resin with good plastic adhesion performance and no crosslink tendencies, it reduces the shrinkage of the adhesive. This assists adhesion by reducing the amount of stress and force caused by adhesive shrinkage that is applied to the substrate/adhesive interface. With less stress at the interface, the adhesion can be greatly improved.

Reactivity

The reactivity of SPF 117 appears high even though not a great amount of functionality is formulated into the adhesive. The inert aldehyde resin, GENOMER* 6083/TP, has a Glass Transition Temperature (Tg) of +35ºC, which makes the system appear to cure quickly, even though the inert resin does not react in the polymer matrix. Once applied, it is fully cured as soon as the acrylate monomers, which are fast curing based upon their relatively high ratio of functionality to molecular weight, and the GENORAD* 40 are cured. To increase reactivity, a formulator would need to add some trifunctional acrylate products to the adhesive or increase the amount of photoinitiator. Conversely, decreasing the functionality would reduce the reactivity in the system.

Viscosity

The viscosity of SPF 117 can be altered by changing the ratio of inert resin to monomer in the adhesive. A greater ratio of GENOMER* 6083/TP to monomer will increase the viscosity, and a lower ratio of GENOMER* 6083/TP to monomer will reduce the viscosity.

UV Curable LA for PET
SPF 253

Flexo laminating adhesive for film, paper, and Al foil in combination with treated PET.

Product	%
GENOMER* 4269/M22	17.0
GENOMER* 7151	45.6
GENOMER* 1122	14.4
Caprolactone Acrylate	19.0
GENOCURE* LTM	4.0
TOTAL	**100**

Properties	
Viscosity (cps or mPa.s)	1050
Reactivity (mJ/cm2)	120

Adhesion Results using T-Peel Test

Substrate Failure results on the following substrate combinations

PET/Paper	PET/PET	PET/Al Foil	PET/OPP	PET/PE

Modifications to SPF 253

T-Peel Property

In SPF 253, the T-Peel performance is dictated by not only the GENOMER* 7151, but also by the GENOMER* 4269/M22 and by the GENOMER* 1122. These products exhibit excellent adhesion on difficult polyolefins. Additional amounts of these products in the adhesive will tend to offer better T-Peel properties.

Reactivity

The reactivity of SPF 253 can be accelerated with additional functionality being formulated into the system. The monofunctional monomers can be replaced by difunctional acrylate monomers, and the difunctional GENOMER* 4269/M22 can be maximized to increase reactivity in the system. Additional photoinitiator can also be added to the system to increase reactivity. The UV absorbance of certain films, especially PET, can negatively affect reactivity. An Fe-Doped bulb, which emits a greater intensity of longer wavelength UV radiation, is an efficient method of dealing with this problem; however, the system's photoinitiator must adsorb radiation at this altered wavelength. The use of long wavelength adsorbing photoinitiators like 2,4,6-Trimethylbenzoyldiphenylphosphine Oxide (GENOCURE* TPO), GENOCURE* LTM (Proprietary eutectic blend), or Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (GENOCURE* BAPO) is necessary to achieve proper cure using an Fe-Doped bulb.

Viscosity

Additional amounts of low functional acrylate monomer will reduce the viscosity efficiently. In SPF 253, increasing the GENOMER* 1122 and the Caprolactone Acrylate will reduce the adhesive viscosity, while an increase of the GENOMER* 7151 and the GENOMER* 4269/M22 will raise the viscosity.

PSA-Type UV Curable LA
SPF 109

Flexo PSA-type (wet) laminating adhesive with adhesion to a wide variety of substrates.

Product	%
GENOMER* 4188/EHA	26.1
GENOMER* 6043/M22	35.1
GENOMER* 1121	5.6
GENOMER* 1122	5.6
2-(2-Ethoxyethoxy) Ethyl Acrylate	23.6
GENOCURE* LTM	4.0
TOTAL	**100**

Properties	
Viscosity (cps or mPa.s)	630
Reactivity (mJ/cm2)	500

Adhesion Results using T-Peel Test
Results are either substrate failure or are given in N/25mm.

OPP/OPP	7.07	OPP/Met. OPP	2.62
PE/Paper	2.71	PET/Paper	1.24
OPP/Paper	1.42	PET/Al Foil	SF
PE/Al Foil	SF	PET/PET	7.29

Modifications to SPF 109

T-Peel Property

A PSA-type laminating adhesive is very different than a “dry”-type adhesive. The T-Peel properties are dictated by the elastic and adhesive properties of the laminating adhesive. In SPF 109, the GENOMER* 4188/EHA exhibits exceptional elongation properties (384%) and good cohesive strength. This balance of flexibility and cohesion coupled with excellent adhesion attributes produces high peel values in a laminating adhesive. An increase in the GENOMER* 4188/EHA will raise the adhesive’s T-Peel performance even higher. In addition, the combination of GENOMER* 1121 and the GENOMER* 1122 help to enhance both adhesion and strength in the laminating adhesive. The GENOMER* 1121 has a high Tg of +80ºC and can create hard strong products. Conversely, the GENOMER* 1122 has a Tg of -3ºC and is extremely flexible with good adhesion characteristics. When used in combination, the two monomers provided better T-Peel values than when used as the sole diluent as their respective contrasting properties are blended to create a well-balanced adhesive.

Reactivity

The reactivity of the SPF 109 is very low, as the formulation contains only monofunctional products and an inert resin (GENOMER* 6043/M22). This is typical of an Energy Curable PSA. Adding difunctional Urethane Acrylates or acrylate monomers will increase the reactivity, but it will also negatively affect the tack and adhesion properties of the adhesive. Additional photoinitiator will help a bit, but low reactivity is the inherent curse of an Energy Curable PSA.

Viscosity

The viscosity can be altered by changing the ratio of oligomer to acrylate monomer. The greater the ratio of oligomer to monomer, the higher the viscosity will be. The lower the ratio of oligomer to monomer, the lower the overall viscosity will be.

PRODUCT DISCUSSION

Summary of products included in LA Starting Point Formulations

Product Code	Description	Tg°C	Comments
GENOMER* 4188/EHA	Monofunctional Aliphatic Urethane Acrylate Oligomer	-16	High elongation, excellent elastic properties for high tack and peel.
GENOMER* 4269/M22	Difunctional Aliphatic Urethane Acrylate Oligomer	-15	Good balance of elastic properties and crosslinking
GENOMER* 6043/M22	Modified Polyester Resin	-18	Flexibilizer resin for PSA, low yellowing, excellent adhesion
GENOMER* 6083/TP	Inert Resin	+35	Good flexibility, good adhesion on plastics
GENOMER* 2252/TM20	Epoxy Acrylate	+47	Excellent reactivity, high scratch and chemical resistance
GENOMER* 7151	Carboxyfunctional Polyester Acrylate	+39	Good adhesion on glass and metal
GENOMER* 1121	Isobornyl Acrylate	+80	High Tg, good flexibility, good

			cutting power, good adhesion and moisture resistance
GENOMER* 1122	Aliphatic Urethane Acrylate	-3	High flexibility and low odor, excellent adhesion on plastics
Caprolactone Acrylate	Caprolactone Acrylate	-40	OH functional, good for dual cure systems, low odor, flexible and low Tg
EOEOEA	2-(2-Ethoxyethoxy) Ethyl Acrylate	-53	High flexibility and low shrinkage, low Tg, excellent cutting power
TPGDA	Tripropylene Glycol Diacrylate	+62	Low volatility, good cutting power
DPGDA	Dipropylene Glycol Diacrylate	+104	Low volatility, good cutting power, high Tg
TMPTA	Trimethylolpropane Triacrylate	+62	Excellent reactivity, good offset properties, chemical resistance, low volatility
GENORAD* 40	Adhesion Promoter	-	Adhesion promoter on metal, glass and plastics
GENOCURE* DMHA	Dimethylhydroxyacetophe none	-	Low yellowing, liquid photoinitiator
GENOCURE* LTM	Liquid Photoinitiator Blend	-	Eutectic blend liquid photoiniator with good balance of surface and through cure, non-yellowing

Summary of plastic films used in testing

OPP	Bicor 50LBW	Atlantic Printing Co.
PET	PE-2	Chemsultants
PE	1150HD	ExxonMobil Films Business
Metallized OPP	70 MET	ExxonMobil Films Business
Paper	Semi-Gloss	Marathon International

Conclusion

The four laminating adhesives discussed here are each quite different when examined side by side, and their results show such formulating differences. The goal of these Starting Point Formulations is to exhibit different formulating tools and methods that our formulating customers can use when faced with the task of creating Energy Curable laminating adhesives. Please note that any changes in functionality or type of chemistry used can have drastic effects on the resulting adhesive. Small changes can sometimes go a long way when formulating adhesives.

References

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