Radiation-curable laminating adhesives

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Radiation-curable laminating adhesives are finding new aplications in paper, metalized paper, plastic, and foil laminates, in fiber optics, and on glass substrates.

Fast-curing, single-component, radiation-curable laminating adhesives are being used to bond and seal a wide variety of substrates, including paper, glass, plastics, and metal. These adhesives show good retention of strength and durability after curing.

Radiation-curable adhesives provide an alternative to the conventional solvent-based, water-based, and hot-melt adhesives. Conventional adhesives require a long cure time at relatively high temperatures. This has led many prospective users to dismiss these adhesives as impractical, despite their potential benefits in reducing weight, lowering costs, and improving productivity.

Why use radiation-curable adhesives?

The growing interest in radiation-curable laminating adhesives is based largely on three issues: environmental control, process economics, and performance advantages.

Environmental control

The manufacture of conventional solvent-based adhesives produces a great deal of atmospheric pollution. The solvents in these adhesive systems are also flammable and toxic.

Process economics

Conventional adhesives (including hot-melt systems) involve preparation of a base polymer or copolymer in a batch process followed by heating them in an oven to evaporate the solvents. In contrast, the radiation process consists of simply applying a liquid formulation to the substrate, passing it under a radiation source, and then collecting the finished product. This process is significantly easier and more efficient than conventional methods.

Performance advantage

The performance characteristics of radiation-curable laminating adhesives are often superior to those of conventional adhesives. These performance properties include peel strength, shear strength, resistance to solvents, and resistance to migration of plasticizers from plastic substrates.

Radiation-curable laminating adhesives provide many advantages, including:

Fast cure. The adhesive can be fixed in seconds. This curing speed is essential for heat-sensitive substrates, which are protected from distortion by the low processing temperature.

Single-component system. The use of a single-component system allows problem-free, automatic dispensing and eliminates the necessity of metering multiple components.

Reactant-type system. Reactant-type systems do not need a solvent. With no solvents being evaporated, there is a reduction in film shrinkage and the resultant film imperfections.

Heat resistance. Radiation-curable laminating adhesives have good heat resistance. They also retain their strength and durability after curing.

Polymerization by radiation

Polymerization by radiation is similar to the conventional process of thermal, free-radical polymerization that is initiated by peroxide or azo compounds. In an ultraviolet (UV)-curable formulation, free radicals are generated from the photoinitiator upon exposure to UV light. In an electron-beam (EB)-curable formulation, free radicals are generated on the reactive functional sites upon exposure to an EB source. In both formulations, the free radicals initiate polymerization, and curing occurs. Both processes are illustrated in **Fig. 1.**

Acrylic or vinyl monomers polymerize and copolymerize by a free-radical mechanism. Certain polymers can also crosslink when irradiated, forming a graft copolymer in the presence of suitable monomers.

There are two radiation-curing processes currently in use: polymerization by UV and by EB.

Polymerization by a UV process

A UV processor is basically a moving conveyor that passes beneath a UV lamp. The distance between the lamp and the conveyor is a critical factor in the process. A UV processing unit also includes a suitable reflector, a radiation shield, and a cooling system.

The intensity and wavelength of the curing UV radiation must be carefully controlled for optimum results. Mercury

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I. Laminating applications for UV/EB-curable adhesives

Homo laminates	
Bonding of	polyester laminates
	polycarbonate laminates
	polyethylene laminates
	cellulose acetate laminates
	glass laminates
Hetero laminates	
Bonding of	paper to polyester
	paper to metallized polyester
	acrylic sheet to vinyl
	polyester to nylon
	nylon to polycarbonate
	polyester to polycarbonate
	glass to vinyl
	glass to polyester
	glass to polycarbonate
	glass to cellulose acetate

II. Typical properties of UV/EB-curable adhesives

Wet adhesive	
Appearance: Light yellow to reddish clear liquid	
Color (Gardner)	1 - 6
Viscosity @ 25°C, P	10 - 80
Refractive index @ 25°C	1.47 - 1.50
Density @ 25°C, lb/gal	9.2 - 9.5
Unsaturation/100 g	0.20 - 0.26
Cured film	
Hardness (Shore D)	10 - 40
Tensile strength, psi	600 - 1000
Elongation, %	20 - 350
Glass-transition temperature, °C	20 - 45

lamps are the most frequently used source of UV radiation. In the case of face-to-face bonding applications, the light-absorption characteristics of the photoinitiator and the substrate should be examined. Most UV-curable adhesive systems contain a photoinitiator that is effectively cured when the mercury emission line is centered at 366 nm.

For laminating adhesives, care must be taken to ensure adequate light transmission at the wavelengths required by the initiator absorption. Glass bonding is an important application for a UV adhesive. For standard soda glass, the transmission is about 80% at 366 nm. The absorption below 300 nm is completely blocked by the glass.

Polymerization by an EB process

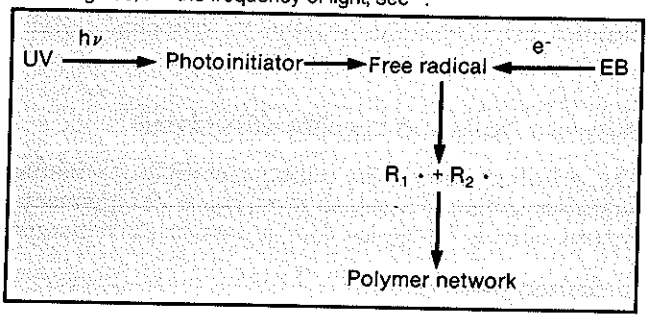
An EB processor consists of three units: a control panel, a transformer capable of stepping up line voltage, and an electron accelerator. The work presented here is based on results obtained using a low-energy EB apparatus. This was an electron curtain type of accelerator that was equipped with a linear filament. The EB processing was performed with the electron accelerator operating at 175 kV and 6-8 mA (the dose rate was 6-8 Mrad), and samples were irradiated under nitrogen at room temperature.

One of the advantages of EB curing is its ability to cure buried layers of 100% solid adhesives. The process allows lamination of a wide variety of paper, film, and foil constructions (*1*, *2*).

The principal components of a radiation-curable laminating adhesive are polymers, monomers, and additives. UV-sensitive adhesives also contain a photoinitiator. The desired properties for specific applications are obtained by properly selecting and balancing the ingredients.

The polymer in a radiation-curable formulation can be a rubber resin, a polyester, or an acrylic resin with an unsaturated double bond. The polymer contributes to the peel strength and the cohesive strength, and it has a strengthening effect in the cured adhesive (*3*). The type of polymer used is determined by its solubility in the monomer mixtures. The amount of polymer to be incorporated in the adhesive depends on the desired viscosity of the composition and on the polymer's molecular weight. Adhesive properties become inadequate below a certain minimum molecular weight (*4*).

1. In an ultraviolet (UV)-curable formulation, free radicals are generated from the photoinitiator upon exposure to UV light. In an electron-beam (EB)-curable formulation, free radicals are generated on the reactive functional sites upon exposure to an EB source. In both formulations, the free radicals initiate polymerization, and curing occurs. R_1 = reactive monomer; R_2 = reactive polymer; h = Planck's constant 6.625 × 10^{-27} erg sec; ν = the frequency of light, sec^{-1}.



The monomers used in radiation-curable adhesives include all the common acrylic and vinyl monomers used in conventional adhesives. Highly functional monomers can also be used in some adhesive systems to increase certain properties via crosslinking and specific functionality.

Additives such as surfactants, antioxidants, and stabilizers are used to improve the performance of the product. The commonly used photoinitiators for use in UV systems include benzophenone, benzoin, and benzoin alkyl ethers. Photoinitiator concentration varied from 0.1% to 3%.

An EB composition is similar to a UV composition with two notable exceptions:

1. The UV composition requires a photoinitiator to generate the free radicals, and the curing reaction proceeds rapidly.
2. The EB-curing process has greater penetration. This increases the choice of substrates that can be used in laminating applications.

III. Peel strength and shear strength of four radiation-curable laminating-adhesive systems on various substrates

Substrate*	System 1 UV	System 1 (EB)	System 2 UV	System 2 (EB)	System 3 UV	System 4 UV
			Peel strength, lb/in.			
Glass/cloth	4.7		4.5		...	...
Glass/mylar	17.7		7.5		...	...
Glass/polycarbonate	27.2		6.5		...	...
			Shear strength, psi			
Glass/glass	1300		1250		280	200
(Heat cycle test)	1030	...	530	...	160	400
Vinyl/mylar	178	...	154	(183)	...	...
Vinyl polycarbonate	214	...	263	...	...	...
Mylar/mylar	207	(166)	153	...	...	...
Mylar/polycarbonate	218	...	165	(175)	...	...
Polycarbonate/polycarbonate	220	(248)	275	...	...	...
Nylon/glass	410	...	570	...	...	...
Nylon/polycarbonate	180	(181)	279	...	...	...
Nylon/mylar	197	...	161	(168)	...	...

*No special surface preparation is required.

IV. Environmental resistance of four radiation-curable laminating-adhesive systems*

	Adhesive system 1	2	3	4
Water & humidity	Fair	Good	Excel.	Excel.
Acetone	Fair	Fair	Excel.	Poor
Toluene	Good	Excel.	Excel.	Excel.
Methyl ethyl ketone	Fair	Good	Excel.	Poor

*Adhesives were immersed in solvents for 24 h.

Evaluation of performance

The emergence of substrates with smooth, nonporous surfaces have created problems for adhesive formulators. Plastics, which have low-energy surfaces, and glass were particularly challenging. With the advent of new EB/UV-curable laminating adhesives, high bond strengths as well as superb bonding integrity at low adhesive weights can be achieved. The use of radiation-curable laminating adhesives has grown rapidly.

Table I lists the applications that have been successfully performed in our laboratory. The adhesives were evaluated based on the following tests:

Peel strength. Peel strength was evaluated using ASTM D-903, which involves applying a soft film substrate to a glass plate and determining the force required to remove the soft film at a 180° angle. Results are presented in units of total load per unit width of bond line. Peel strength is affected by the peeling rate and angle, the thickness of the adhesive, and the backing substrate (*5*).

Shear strength. Shear strength was evaluated using ASTM D-1002. This test measures the maximum shear stress that the adhesive can withstand before failure under tensional loading. Three types of shear failure were encountered: backing failure, clean-release failure, and cohesive failure.

Table II shows the range of typical properties for the UV/EB-curable laminating adhesives that we developed and tested. **Table III** lists the adhesion properties of four UV/EB-curable adhesive systems. **Table IV** shows the environmental resistance of these proprietary products.

System 1 was composed of 30–40% resin and 60–70% mixture of reactive monomers. System 2 contained the same resin system but was formulated with a different combination of monomers. Systems 3 and 4 consisted of 50–60% urethane acrylate oligomer and a blend of monofunctional and difunctional monomers. These adhesive systems were specially formulated for certain applications.

Systems 1 and 2 adhered well to most of the smooth, nonporous surfaces. They showed excellent bonding strength on the glass laminates. System 1 retained about 80% of shear strength after the heat-cycle test (180°F for 24 h followed by -20°F for 24 h). Systems 3 and 4 adhered best to glass and had good moisture and water resistance. System 3 also had the best environmental resistance. No remarkable difference in shear strength was observed between cured samples from UV and EB processing.

Table V compares the performance characteristics of UV/EB-curable laminating adhesives with those of conventional laminating adhesive systems (*6*). In general, the performance of UV/EB-curable laminating adhesives is superior or comparable with the conventional commercial laminating adhesives. The UV/EB-curable systems have the added advantage of a simpler production cycle and reduction of atmospheric pollution, toxicity, and flammability.

There are a growing number of applications for UV/EB-curable laminating adhesives on a variety of substrates, including paper, metalized paper, plastics, fiber-optic materials, and foil laminates. It also appears that radiation-curable adhesives can be used in high-performance dielectric/conductor laminations. This last application is suitable for radiation-curable laminating adhesives because they eliminate the difficulties of (a) evolving the solvent before lamination and (b) controlling

V. Performance characteristics of UV/EB and conventional laminating adhesives

	UV/EB	*Epoxy based*	*Polyurethane based*	*Silicone based*	*Rubber based*	*Hot-melt*
Curing method	Radiation (one component)	Acid/base catalyst (two parts)	Moisture/ amine (two parts)	Heat/ catalyst (one or two parts)	Heat/ pressure (solvent based)	Heat (one component)
Curing condition	RT* Fast	RT* - 350°F Slow Need post cure for ultimate performance; need thorough mixing.	RT* - 200 °F Slow Post-cure mixing	RT* - 300°F Slow Post-cure mixing	RT* - 250°F Slow Post-cure mixing	Over melting point of the base polymer; Slow
Adhesion properties	Good ↓ Excellent	Good ↓ Excellent Peel strength low; adhesion to plastics weak	Good ↓ Excellent	Fair ↓ Good Peel & shear strengths low; adhesion to organic substrates weak	Fair ↓ Good	Good Loss of strength at elevated temperature and tends to be brittle at low temperature
Chemical resistance	Excellent	Excellent	Excellent	Excellent	Poor	Poor
Heat resistance	Good	Excellent	Good	Excellent	Fair	Poor
Environmental hazard	Low	Low	Health hazard from isocyanate	Emission of by-product	Emission of solvent	Low
Materials and operation cost	Moderate	High	Low	High	Low	High

*Room temperature

adhesive tack before combining the substrates.

Summary

The future of radiation-curable laminating adhesives appears to be bright. Faced with increasingly stringent environmental laws for solvent emission and increasing energy costs, many potential users are considering the significant advantages of curing adhesives by exposure to ultraviolet light or to a source of electron beams.

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