

# Accelerated electron-cured, hot-melt pressure-sensitive adhesives provide improved plasticizer and heat resistance

Woody Bradford

*Elastomeric hot-melt pressure-sensitive adhesives exposed to accelerated electrons will be useful in labeling flexible polyvinyl chloride materials, on polyvinyl chloride as a face stock, and in various industrial applications requiring low thermoplasticity.*

Ionizing radiation can cause polymer chain scission and degradation in some pressure-sensitive adhesives (PSAs). With properly polymerized or formulated adhesives, however, such radiation is an effective means of introducing property-enhancing cross-links, which improve performance. These improvements are those which are associated with increased molecular weight, e.g., high cohesive strength, lower thermoplasticity (resulting in higher cohesive strength at elevated temperatures), and better chemical resistance. Both ultraviolet and accelerated electron (EB) sources are in commercial use for such purposes, and extensive R&D is focusing on additional applications.

Such radiation cured pressure-sensitive adhesives have been topics at a number of recent conferences and seminars. These include the various annual and regional meetings of RadTech International and privately sponsored seminars such as the Radiation Curing Technology and Radiation Cured Products Seminar held by Satas and Associates in Boston in 1989. Background information on the processes and adhesive types used and the results of the irradiation can be found in recent papers.<sup>1,2</sup>

A new family of radiation-curable pressure-sensitive adhesives is based on a formulated, elastomeric approach designed for hot melt coater application. These EB-cross-linking adhesives have two properties of particular

interest to manufacturers of pressure-sensitive coated materials:

1. Resistance to chemical plasticization
2. High cohesive strength at both standard and elevated temperatures.

## Plasticizer-resistant PSAs

Plasticizers are added to normally rigid or brittle materials to improve flexibility and expand their range of potential use. In the area of pressure-sensitive adhesive bonding, polyvinyl chloride (PVC) is the type most often seen. Depending on the chemistry and concentration of plasticizer added, rigid PVC resins can be manufactured to varying degrees of flexibility. At one extreme, for semi-rigid molded goods, they are produced with only a slight reduction in modulus; at the other extreme, highly flexible film materials for use in label applications are produced.

The plasticizers can be monomeric, such as dioctylphthalate (DOP), or polymeric, such as low-molecular-weight polyesters. Mixtures of monomeric and polymeric grades are often used to tailor properties. The plasticizers, regardless of type, are present as physical mixtures with the PVC resin, not chemically bonded. As a result, they are extractable to varying degrees, as shown in **Fig. 1**. Extraction occurs when a plasticized PVC surface contacts another material having equal or greater compatibility with the particular plasticizer. The problem is especially severe with low-viscosity liquid plasticizers. These grades tend to be mobile and highly migratory.

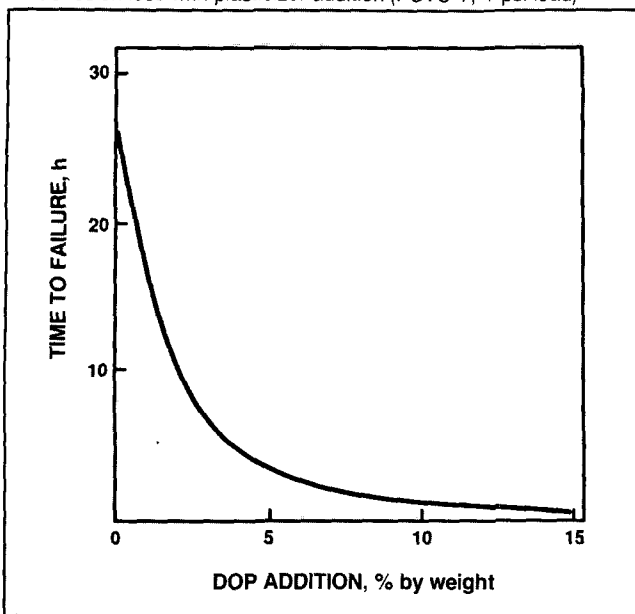
In more cases, the compatibility of pressure-sensitive adhesives favors migration of PVC plasticizers. The softening effect of absorption of these plasticizers into the adhesive film varies with the chemistry of both the plasticizer and the adhesive. In many cases, they can reduce cohesive strength of a PSA to below the minimum

<sup>1</sup>Fries, J., Radiation Curing and Sterilization of Adhesives, RadTech '88—North America, RadTech International, Northbrook, Ill., 1988, p. 440.

<sup>2</sup>Ellerstein, S. M. and Lee, T. K. P., Radiation Curable Pressure Sensitive Adhesives, RadTech '88—North America, RadTech International, Northbrook, Ill., 1988, p. 461.

Bradford is specialty adhesives technical service chemist at National Starch and Chemical Co., Box 6500, Bridgewater, N.J. 08807.

1. Cohesion loss with plasticizer addition (PSTC-7, 4-psi load)



useful level. The effect is easily demonstrated by adding varying amounts of plasticizer to a PSA formulation and then measuring cohesion as a function of concentration. Table I shows this effect for dioctylphthalate added to a rubber-based paper-label-grade PSA.

Much of the R&D conducted over the years on upgrading pressure-sensitive adhesives has focused on more plasticizer-tolerant grades. The first solution acrylic copolymer PSAs, introduced in the mid-1950s, were justified in part on this basis. Earlier rubber-based grades were excessively softened by migratory plasticizers. An interim approach, using polyvinyl ether resins, was better, but these in turn were quickly superseded by the still better acrylics.

Acrylics continue to be the standard. They have evolved from the original thermoplastics to today's chemically cross-linking systems. Performance of some current solution and waterborne grades is acceptable for many applications. Limitations remain, however, especially on highly flexible surfaces in which monomeric plasticizers are used. Examples of these surfaces include soft-sided PVC luggage, PVC-surfaced notebooks and binders such as photo albums, and some PVC label stocks. Face materials such as decorative wood grains and the higher-quality grades of migration-resistant decal films have less effect on correctly designed PSAs, but may still cause significant loss in performance.

In addition to the drawbacks of current solution and waterborne PSAs, hot-melt grades for PVC in both rubber-resin and acrylic form have limited resistance to the destructive effects of plasticization.

In response to this need, a new 100% solids cross-linkable PSA has now been developed with exceptional resistance to plasticizer migration. Based on a specially-designed block copolymer, this adhesive is designed for application by currently used hot-melt coaters, with the addition of an EB radiation unit for cross-linking.

I. Effect of EB on peel and tack

|                                           | Dose, megarads |     |     |
|-------------------------------------------|----------------|-----|-----|
|                                           | 0              | 2.5 | 5.0 |
| 180° peel, oz./in.<br>(PSTC-1)            | 55             | 53  | 50  |
| Tack, oz./in. <sup>2</sup><br>(TLMF loop) | 52             | 52  | 53  |

Note: Adhesive transfer coated at 1 mil onto 2-mil crystallized polyester.

II. Cohesive strength retention after EB cure

|               | Dose, megarads |     |      |
|---------------|----------------|-----|------|
|               | 0              | 2.5 | 5.0  |
| 4-psi hold, h | 5              | 24  | 100+ |

Note: Adhesive transfer coated at 1 mil onto 4-mil decal-grade PVC. Construction aged 3 days at 140°F prior to testing.

## EB cross-linking: effect on properties

One of the advantages of the EB cure technique is the relatively minimal effect on tack and peel strength. Table I shows the results of EB irradiation on peel value and tack, using inert face materials.

To evaluate cohesive strength retention upon plasticization, coatings were made on 4-mil decal-grade PVC film. These were irradiated and then aged three days at 140°F to accelerate plasticizer migration. The results shown in Table II demonstrate the improvement obtained from as little as 2.5-megarad exposure.

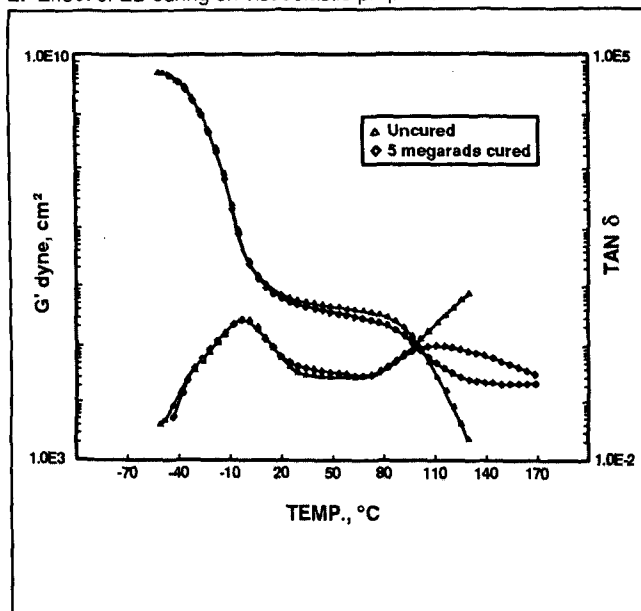
Visual and tactile confirmation of resistance to plasticization can be shown in labeling of highly plasticized surfaces. After aging in place, porous-face stock labels made with the new EB-irradiated PSA exhibit no face stock staining. Nonirradiated controls of the same adhesive, as well as conventionally used hot-melt and waterborne PSAs, are moderately to severely stained.

The applications discussed here involve permanent labels and other uses where high peel strength is needed. Another application—mounting of sanding discs on flexible, PVC surfaced platens—requires the ability to cleanly remove the label after use. This is a particularly difficult requirement since both a highly-plasticized surface and frictionally generated heat are involved. The new EB-cured hot-melt PSA is able to meet this challenge.

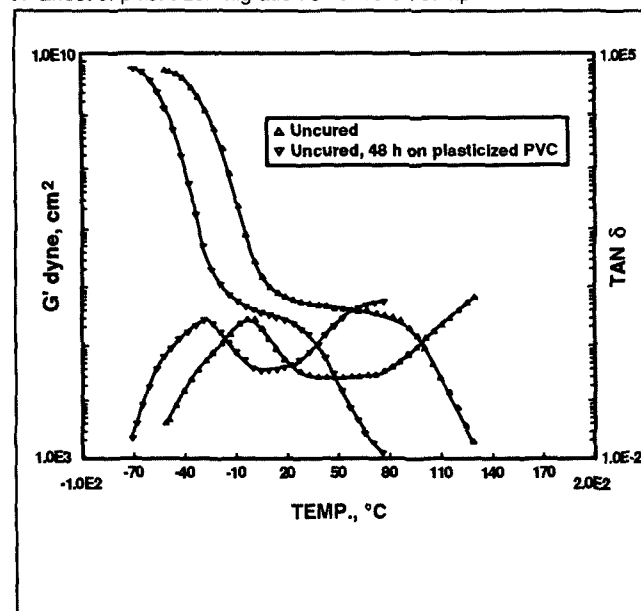
The new hot-melt PSA was transfer coated at 1 mil onto 2-mil crystallized polyester, irradiated with EB, and bonded to the PVC surface. The assemblies were then aged for three days at 120°F to accelerate plasticizer migration. At no dose, the mounted strip is very gummy and leggy on removal. After 5 megarads, the strip removes cleanly without legs or residue.

The effect of curing on this system is shown clearly by viscoelastic property curves before and after cure. The  $G'$  (elastic modulus) and  $\tan \delta$  (ratio of loss modulus to elastic modulus) curves shown in Fig. 2 were generated by a Rheometrics® dynamic analysis. As tests confirmed, peel

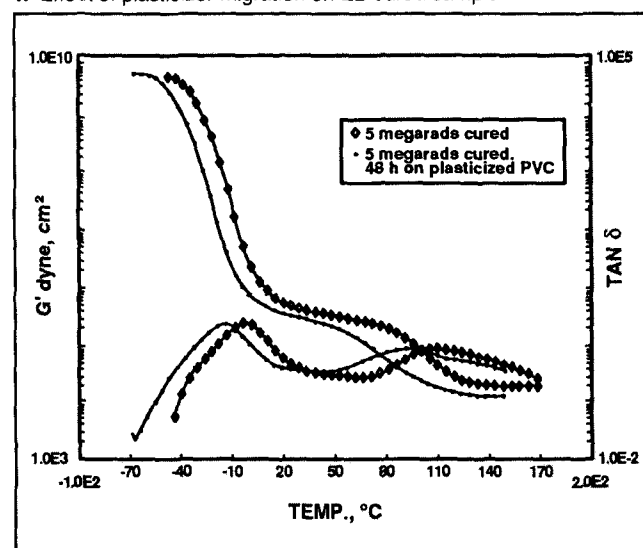
2. Effect of EB curing on viscoelastic properties



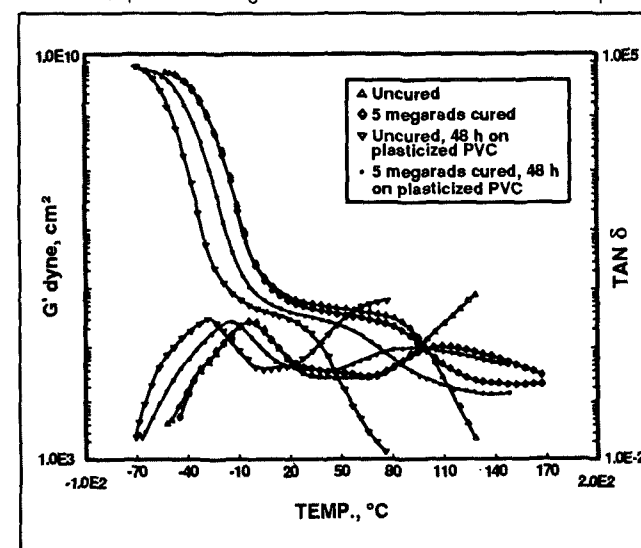
3. Effect of plasticizer migration on uncured sample



4. Effect of plasticizer migration on EB cured sample



5. Effect of plasticizer migration on EB cured and uncured samples



and tack are depicted as remaining unchanged, while cohesive strength is greatly enhanced by curing.

Figure 3 shows the effect of plasticization on the uncured adhesive. Cohesive strength is lost, and the  $\tan \delta$  shifts down in temperature as the material is softened by the plasticizer.

Figure 4 shows the far less dramatic effect of plasticization on the cured adhesive. Cohesive strength is only slightly diminished, and the shift in  $\tan \delta$  is significantly reduced.

Figure 5 combines Figs. 3 and 4 for a direct comparison.

In a variety of PVC applications backed by standard tests and viscoelastic comparisons, this PSA approach appears to fill a longtime gap in the pressure-sensitive arsenal.

### High-cohesion, heat-resistant PSAs

The hot-melt plus EB system described above is proving useful where high cohesion and good heat resistance is needed. Products having these properties are demanded in industrial assembly and mounting applications using two-side coated tapes and transfer films. End uses include name plates, auto side molding, and vibration and sound dampening. High-performance, cross-linked acrylic-solution PSAs are the current preferred type for these uses. Conventional hot-melt PSAs are not used because of their extreme thermoplasticity. Even those with excellent cohesion at room temperature lose most of this strength above 140°F.

Table III gives the results of EB irradiation on elevated-temperature cohesive strength for one of the new hot-melt

products. Cohesion retention at 160°F is significantly improved by a 5-megarad dose.

As discussed, dynamic mechanical analysis techniques are useful in quantifying and optimizing adhesives of this type (Fig. 2).

### Conclusion

A new family of EB radiation-curable, hot-melt pressure-sensitive adhesives based on a formulated, elastomeric approach is currently available. These products provide manufacturers of hot-melt pressure-sensitive coated materials with improved shear and heat resistance as well as resistance to the detrimental effects of plasticizer migration. □

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### III. Elevated temperature cohesion

|                                    | Dose, megarads |     |     |
|------------------------------------|----------------|-----|-----|
|                                    | 0              | 2.5 | 5.0 |
| 2-psi hold at 160°F<br>(PSTC-7, h) | 0.5            | 5   | 24  |