

## UV-CURABLE RELEASE COATING AND ADHESIVE FORMULATIONS CONTAINING VINYLEETHERS



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Arvind M. Mathur, James A. Dougherty, and John McKittrick  
International Specialty Products

1361 Alps Road, Wayne, NJ 07470, USA

Phone: 1-973-628-4000; Fax: 1-973-628-3886; e-mail: amathur@ispcorp.com

and

Richard Eckberg

GE Silicones

260 Hudson River Road, Waterford, NY 12188, USA

Phone: 1-518-233-2200; Fax: 1-518-233-2367; e-mail: Richard.Eckberg@gepex.ge.com

### ABSTRACT

Vinylether monomers offer unique properties for UV/EB curing due to their efficiency as reactive diluents and their ability to undergo both cationic homopolymerization and free-radical copolymerization. The benefits derived from the inclusion of vinylethers into commercial UV-curable epoxysilicone formulations include viscosity reduction, improved cationic photoinitiator miscibility, and lower costs. The addition of up to 60 wt.% of monovinylethers to epoxysilicone systems maintains the release performance, resulting in high-performance coatings and valuable cost savings. On the other hand, divinylethers may be used to impart a controlled release behavior to the epoxysilicone systems. Vinylethers may also be used in the formulation of acrylate-free pressure-sensitive adhesives and laminating adhesives. In this paper, we have first elucidated the advantages offered by the inclusion of vinylethers in UV-curable release coatings, followed by a discussion of UV curable pressure-sensitive and laminating adhesive formulations based on vinylethers.

### INTRODUCTION

Most commercial radiation curable release coating formulations are based on polydimethylsiloxane (PDMS) resins that have been functionalized with polymerizable acrylate or epoxy groups. The photoinduced free-radical polymerization of acrylate-functional silicones is commonly used and numerous patents exist on this technology.<sup>1</sup> Free radical polymerizations are inhibited by the presence of oxygen and the high oxygen permeability of silicones amplifies this effect. Thus, commercially acceptable cure speeds are best obtained with expensive nitrogen inerting. Cationically curable epoxy-functional silicones<sup>2,3</sup> are also now commercially available. These coatings cure rapidly with UV exposure and, unlike free radical polymerizations, cationic photopolymerization is not inhibited by the presence of oxygen thus eliminating the need for nitrogen inerting. Cationically curable vinylether-functional silicones are also under active development.<sup>4</sup> In each of these systems, a reactive diluent is often desired to improve performance and optimize physical properties. However, the choice of monomer is severely limited by the poor compatibility of many commonly used diluents with silicone fluids.<sup>5</sup> The ability of vinylethers (VEs) to lower viscosity and costs of silicone acrylate formulations has been recently studied, and formulations based primarily on vinylethers containing small amounts of silicone acrylates, cured by a dual (free-radical and cationic) cure scheme, have also been reported.<sup>6</sup> Further, silicone-free UV-curable release coatings that offer tight release behavior and are based entirely on vinylethers have also been proposed by Dougherty *et al.*<sup>7</sup>

GE Silicones introduced the first commercial cationic UV cure release system, consisting of cycloaliphatic epoxy functional PDMS polymers and compatible photoacid-generating iodonium catalyst packages, over ten years ago.<sup>2,8</sup> These systems meet most performance objectives, but the high organofunctional content (epoxy content) needed for fast UV cure results in photocured release coatings that tend to provide 'zippy' and tighter release than that observed from analogous addition-cure solvent-less silicone formulations. A high polar cycloaliphatic epoxy group content in otherwise nonpolar PDMS also causes increased viscosity compared with linear PDMS of the same chain length. In addition, the non-polar nature of epoxy-silicones even with high organofunctional content limits the miscibility of most commercial onium salt photoinitiators. While the cost of a 1 micron thick silicone coating is but a minor contributor to the total cost of a release liner or final product prepared therefrom, the converting industry is fiercely competitive, so any cost reduction in coating material is desirable. Though vinyl ether monomers are not very inexpensive, they are less costly than commercial epoxy silicone polymers, and hence their use as additives does provide for raw material cost reduction for the end user.

In this paper we have addressed *some* of these issues and have demonstrated that vinyl ethers effectively lower viscosity, enhance photoinitiator miscibility, and contribute to release properties in cationic formulations based on epoxy silicones. Our experimental efforts were primarily focused at investigating the utility of vinyl ethers as performance-enhancing additives in epoxy silicone systems. First, we confirmed that monofunctional VE's were miscible with the epoxysilicones and can be used as reactive diluents to lower viscosity of coating baths and improve coating quality. Improvement in the miscibility of the cationic photoinitiator was also demonstrated without a significant impact on release performance. Second, we quantified the effect of a bifunctional monomer on increasing the release (as a controlled release additive), both with normally low-release epoxysilicones, and as a 'tight release amplifier' with a tight release epoxysilicone. Thirdly, we explored the use of high concentrations of VE monomers in coatings based on high viscosity epoxysilicone polymers. The resulting formulations exhibited viscosities of the same range as conventional solvent-free thermal and UV curable silicone release agents and could therefore be readily applied using the same coating techniques.

Our investigation of vinyl ethers in UV/EB-curable adhesives was motivated by the knowledge that vinyl ethers are effective in adjusting viscosity and increasing the cure speed in UV/EB curable surface coatings for different substrates including wood, plastic, and metal. The excellent adhesion to this wide variety of substrates suggested that these formulations might also be useful as pressure sensitive (PSA) and laminating adhesives. Furthermore, there are numerous literature references to the use of polyvinyl ethers in PSA applications.<sup>9</sup> The availability of cationic photoinitiators with excellent hydrocarbon solubility<sup>2,10</sup> and the expanded availability of vinyl ether monomers<sup>11</sup> should also enable the extension of this technology to UV and EB curable PSA's. We investigated cationically curable UV/EB pressure-sensitive adhesives formulations based on a low Tg monovinyl ether, a divinyl ether crosslinker, and a tackifying resin. The discussion on UV-curable laminating adhesive formulations is focussed on vinyl ether-containing formulations based on a broad range of cure chemistries including, cationic, free-radical, charge transfer, and hybrid.

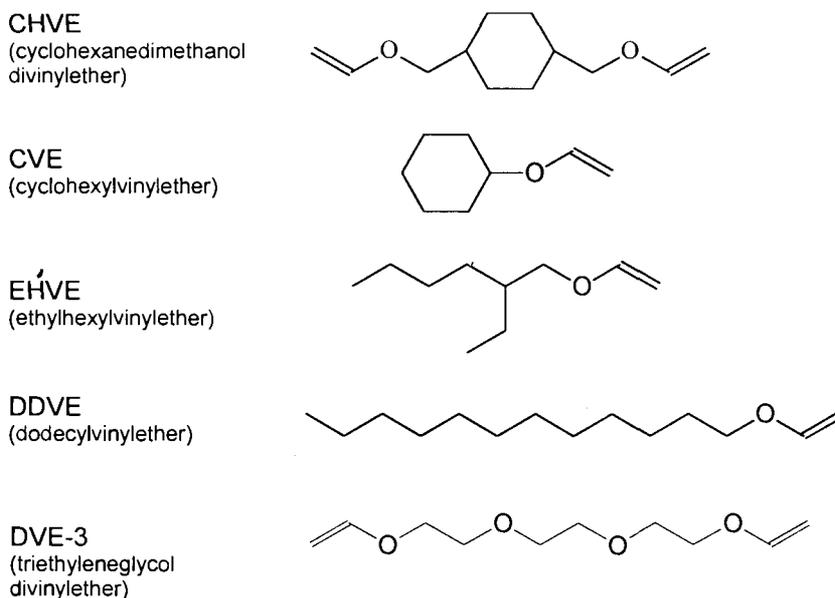
## RAW MATERIALS

The vinyl ether monomers used throughout this study were obtained from International Specialty Products (Figure 1). The epoxy functional silicones and cationic photoinitiator used in the release coating study were obtained from GE Silicones and are described as follows:

- UV9300 – lightly crosslinked low viscosity (300 cSt) epoxy silicone with epoxy-equivalent weight (EEW) of 950 used for common low-release applications.

- UV9315 - low viscosity (300 cSt) low-release linear cyclohexylepoxy-functional PDMS with an EEW averaging 1100.
- UV9400 - analogous low viscosity (250 cSt) epoxysilicone, but with an EEW averaging 1450 (and hence less epoxy content than UV9315).
- UV9430 - tight release epoxysilicone product that is a blend of an epoxy-functional 'Q' resin with a linear epoxy-stopped PDMS<sup>12</sup> with a viscosity of 500 cSt and an EEW of 1600.
- UV9425 - high molecular weight (viscosity: 4000 cSt) linear PDMS polymer with an average EEW of 1050.
- UV9500 - special premium release epoxysilicone blended product described in US Patent 5,397,813 (Eckberg and Griswold, 1993) with a viscosity of 400 cSt and EEW of 1100, designed for premium release versus the most aggressive acrylic crosslinkable adhesives.

(All epoxysilicone polymers were prepared as taught in US Patent 5,391,676 to Eckberg and Agars, 1995). The photocatalyst solution used to promote UV cure of the epoxysilicone coatings was UV9380C. UV9380C consists of about 45% active bis(4-alkylphenyl)iodonium hexafluoroantimonate (where 'alkyl' = a complex mix of linear and branched chain C8-C14 aliphatic groups) and an isopropylthioxanthone (IPTX) photosensitizer in an alkylglycidyl ether reactive diluent. The active iodonium salt component of this product was first described in US Patent 4,279,717 (Eckberg and LaRochelle, 1981).



**Figure 1.** ISP's RAPI-CURE vinyl ether monomers used in this study.

Polyethylene-kraft liner (PK) was furnished by Thilmany Co. and Melinex® 505 polyethylene terephthalate (PET) film was obtained from ICI. Cold rolled steel panels were obtained from the Q-Panel Company. Polyethylene terephthalate (PET) film, glass microscope slides, adhesive tapes manufactured by the 3M Company, Tesa Corp., and Johnson & Johnson were obtained from local vendors.

The iodonium salt cationic photoinitiators for the adhesive formulations were obtained from GE Silicones (UV9380C), Union Carbide Corp. (UVI-6990), and 3M Company (FX-512); while the free-radical photoinitiators were obtained from Ciba Specialty Chemicals. The cycloaliphatic epoxy resin, UVR-6110, was obtained from Union Carbide Corp. An

unsaturated polyester resin, UV 15-156, was obtained from Cargill. Acrylate resins were obtained from Sartomer Company. The silicone surfactant, DC-193, was obtained from Dow Corning Corp. while the hydrocarbon resin, Regalrez<sup>®</sup> 1085, was obtained from Hercules Inc. The stabilizer, t-butyl hydroquinone, was obtained from The Aldrich Chemical Co.

## **TEST METHODS**

### **Release Coating Formulations**

The data on UV-curable epoxy silicone release coatings presented first were obtained from trials conducted at Black Clawson Machine Co. in Fulton, NY, under the supervision of personnel from GE Silicones. The 18-inch B-C pilot coating line was used to coat polyethylene-kraft liner (PK) furnished by Thilmany Co. with experimental and control epoxysilicone and epoxysilicone/VE blends. Cure was achieved in air by exposure to one or two banks of Fusion Systems 600 watt/in 'H' lamps mounted immediately following the 5 roll film-splitting coating station. The samples of cured silicone-coated liner were subsequently laminated with TESA 7475 acrylic test tape or with Ashland 1085 solvent-borne acrylic PSA plus paper face stock to create 2 inch wide tapes. The cured coating samples were aged for 2 weeks prior to lamination with Ashland 1085 solvent-borne acrylic PSA, while the TESA 7475 acrylic test tape was laminated to the coatings within minutes of cure at Black Clawson. Release and aged release of the laminates, aged under ambient conditions (23°C, 50% relative humidity), was measured by recording the force required to peel the silicone coated liner from the adhesive laminate at an angle of 180 degrees using a ZPE1000 high speed release tester. The release was reported as the average of three trials and typical measurement errors were found to be less than 5%. To demonstrate the utility of EHVE and DDVE for improving catalyst miscibility with a commercial epoxysilicone, 2 parts of UV9380C catalyst product were mixed with 100 parts of UV9400 and UV9400/VE formulations. The catalyzed mixtures were then analyzed for turbidity using an HF Scientific Model DRT100B Turbidimeter.

Proof-of-concept release coating formulations investigated at ISP were prepared by mixing the components in an amber vial. The compatibility of vinyl ethers in silicone fluids was determined by blending the desired ratio of components under moderate heat. The mixtures were then allowed to stand overnight and observed in the morning for any sign of phase separation. The viscosity of compatible blends was measured at 25°C using a Brookfield LVT viscometer. A uniform coating of the desired thickness (0.3 mils) was then applied to the PET substrate using a #3 Mayer bar applicator. The liquid coating was cured by exposure to UV irradiation using either an AETEK Model QC 1202A/N UV Processor containing two 200 Watt/inch medium pressure mercury vapor lamps or a Fusion System Irradiator containing one 300 Watt/inch "H" bulb. Quantitative measurements of release and subsequent adhesion were performed on a Gardner Slip/Peel Tester. Coatings were cast on the PET substrate and cured by UV exposure. After 24 hours, the specified tape was applied to the surface and a five-pound rubber roller was rolled over the tape 5 times. Release was determined by measuring the force, in grams per linear inch, required to remove the tape at an angle of 180 degrees. After the tape was removed from the release coating, the subsequent adhesion was determined by reapplying the tape to a clean steel panel, rolling 5 times with the rubber roller, and again measuring the force required to remove the tape at an angle of 180 degrees. For each sample the mean of 5 trials was reported and typical experimental error was observed to be within 5%. Aged release was determined by placing the cured sample in an oven at 70°C for 20 hours prior to applying the test tape and measuring the release as described above.

### **Adhesives Formulations**

All formulations were prepared by mixing the components in an amber vial at room temperature. For the PSA studies, each formulation was applied to a 2 mil polyester film by

hand drawdown using a #12 Mayer bar. Samples were cured by exposure to UV irradiation of 1000 mJ/cm<sup>2</sup> using either the AETEK Processor or the Fusion System Irradiator containing the "H" bulb. Unless otherwise noted, samples were post cured at 70°C for a minimum of 15 minutes. Tack was measured in grams using a Testing Machines Incorporated Probe Tack tester with a dwell time of 0.2 seconds and a speed of 0.1 cm/sec. A minimum of 5 trials was conducted on each sample and the mean reported in grams/cm<sup>2</sup>. Peel strength was measured using a Gardner Slip/Peel Tester. Adhesives were cast on polyethylene terephthalate films and cured as described above. One inch wide strips were cut, applied to a steel substrate, and rolled with a 5 pound rubber roller 5 times. The force required to remove the tape at an angle of 180 degrees was measured in grams. A minimum of 5 trials was conducted on each sample and the mean reported. Shear strength was determined by contacting a one-inch square at one end of a cured PSA coated polyester strip to a stainless steel test panel leaving the other end of the strip free. The test panel was then rolled with a 5 lb rubber roller 5 times and attached to a rack in the vertical position. A 500 g weight was attached to the free end of the coated strip and the elapsed time for each strip to separate from the test panel was recorded. Unless otherwise noted, the experiment was terminated after 24 hours. Formulation viscosity was measured at 25°C using a Brookfield LVT viscometer.

For laminating adhesives, the formulation was applied to one substrate, the second substrate was placed on top, and was then pressed together to remove any air bubbles. Laminates were cured by exposure to UV irradiation of 1000 mJ/cm<sup>2</sup> using either an AETEK Model QC 1202A/N UV Processor or a Fusion System Irradiator containing an "H" bulb. Lap Shear was determined using an Instron testing procedure in accordance with ASTM D 1002. Fixture time was determined as described in the literature.<sup>13</sup> For measurement of fixture time, laminates were prepared as described above and exposed to UV light using a UVEXS Co. SCU 110 UV lamp operating at 13 mW/cm<sup>2</sup>. The fixture time recorded was the shortest UV exposure needed to prepare a laminate capable of suspending a 1 kg weight.

## RESULTS AND DISCUSSION

### UV-Curable Release Coating Formulations

#### *Vinylethers as Reactive Diluents and Photoinitiator Compatibilizers*

Compatibility with the oligomer system is a key requirement of any reactive diluent. This is particularly true with silicone resins where the choice of diluent is severely limited by poor miscibility. Each of the vinylethers shown in Figure 1 was found to be an effective reactive diluent and completely miscible (in all ratios) with various epoxy functional silicones. The viscosity decrease obtained using four vinylethers as diluents for a typical epoxy functional silicone (UV9300) is shown in Figure 2.

The solvency power of EHVE and DDVE was also confirmed at GE Silicones by observing complete miscibility of EHVE, DDVE, and CHVE in several epoxysilicones. For example, a batch of UV9400 epoxysilicone (EEW = 1507) with an initial viscosity of 278 cSt was mixed with varying amounts of the VE monomers and the kinematic viscosity determined using Ostwald tubes at 25°C. The results obtained are presented in Table I, and it may be observed that the viscosity reduction obtained with EHVE was marginally greater than that with DDVE. Further, to demonstrate the effectiveness of vinylethers in enhancing cationic photoinitiator miscibility, turbidity measurements were performed on various UV9400/VE formulations containing 2 parts by weight of UV9380C. Results of the turbidity tests are shown in Figure 3. We observed that catalyzed baths with turbidity greater than 100 tend to be unstable on storage, while turbidity greater than 1000 indicated gross immiscibility.

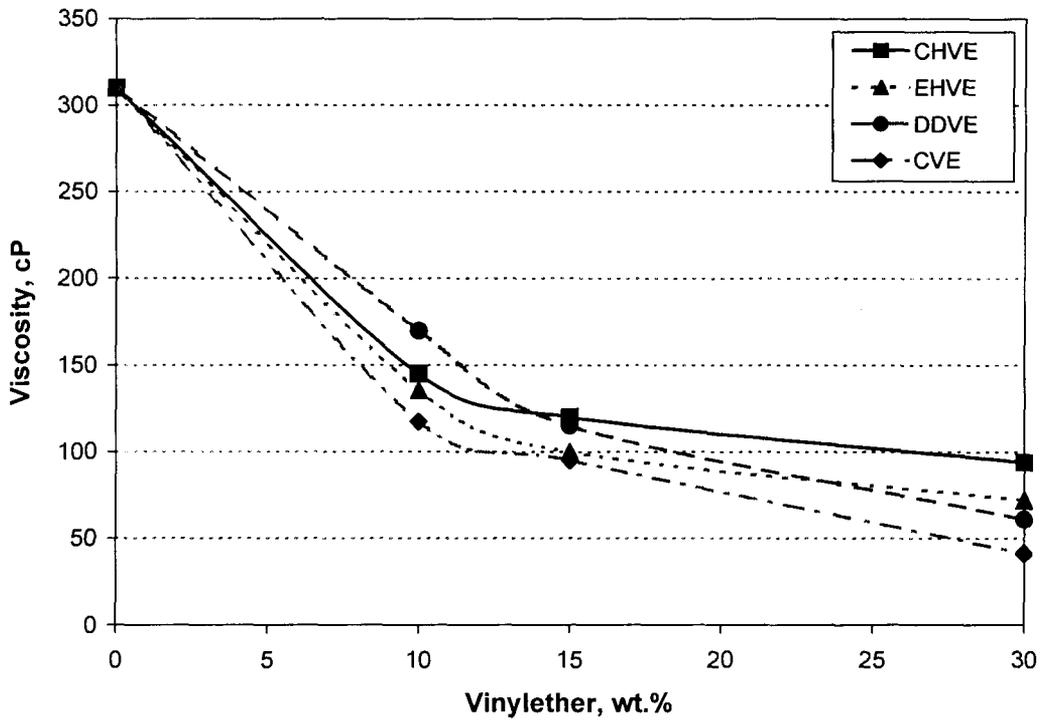


Figure 2. Brookfield viscosity of various vinylether/UV9300 blends.

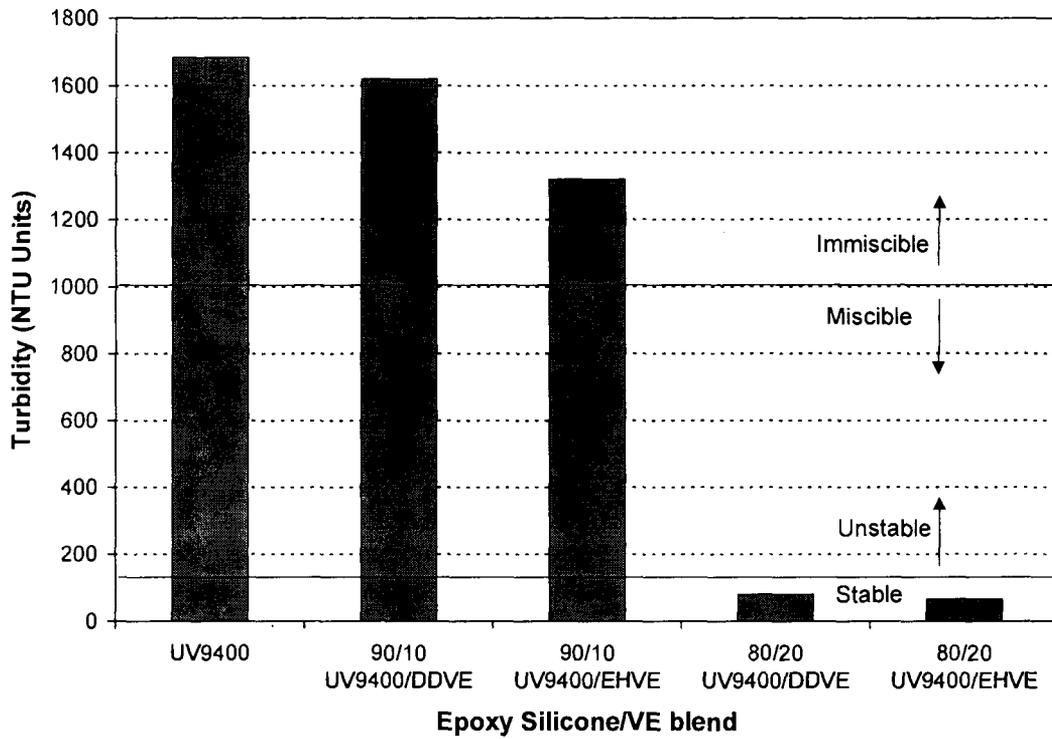


Figure 3. Turbidity measurements for UV9400/VE blends containing 2 parts UV9380C.

**Table I.** Kinematic viscosity of various UV9400/VE blends

Wt. % VE	Viscosity (cSt)	Viscosity (cSt)
UV 9400/VE blend	UV9400/DDVE blend	UV9400/EHVE blend
0	278	278
4	209	204
8	171	154
12	139	117
16	120	97
20	102	78

As seen in Figure 3, formulations containing 20 wt.% of DDVE and EHVE exhibit turbidity of less than 100 NTU units indicating enhanced miscibility. Further, shelf stability of catalyzed baths is increased to at least 3 months with the addition of 10-20% of DDVE or EHVE. Iodonium and sulfonium salt photocatalysts are inherently polar materials bearing localized charges on a cation and an anion. Their miscibility with nonpolar curable materials such as organic monomers, oligomers and organofunctional silicones, is always an issue in the use of UV curable cationic systems. Since the active bis(4-alkylphenyl)iodonium hexafluoroantimonate component of the commercial UV9380C product is not completely soluble in epoxysilicone polymers with EEW greater than 1000, end-users of these formulations may experience problems when catalyzed baths are retained for extended periods of time. Solutions to this problem have included the addition of aromatic and polyether carboxylates into the epoxysilicone structures, and the design of iodonium catalysts with new exceptionally large charge-diffusing counterions. However, these modifications result in higher-cost functional silicones. Due to the complete miscibility of lower-cost vinyl ethers with organofunctional silicones and onium-salt photocatalysts, inclusion of these monomers in the epoxysilicone polymer systems results in significant handling and performance benefits.

#### Vinylethers as Additives for Cost-Performance Enhancement

Shown in Figure 4 and 5 are release performance data, measured against the TESA 7475 tape and the Ashland 1085 tape respectively, demonstrating the effectiveness of EHVE and DDVE as cost-performance enhancing additives with UV9400. The release data presented in Figures 4 and 5 were obtained for coated samples prepared at the Black Clawson facility in which each coating bath consisted of 1 part of UV9380C catalyst added to 100 parts of the UV9400/VE blend. The coating line-speed was set at 250 meter/min. with cure obtained by one bank of focused 600 watt/in 'H' lamps. A coatweight of 1.1 g/sq. meter (total coating including silicone and organic components) was targeted in these trials. Release data using the reference test tape was obtained after successive aging of each sample of the cured coating.

These results indicate that the release behavior obtained is broadly comparable to that of the control UV9400 system and is marginally sensitive to the type of adhesive tape used for evaluation. However, when comparing the formulations incorporating DDVE to those including EHVE it can be observed that the EHVE-diluted systems demonstrate little or no change in the release behavior compared to the control. The formulations containing DDVE demonstrate a marginal increase in the level of release as the DDVE content is increased. Further, in these DDVE systems the aged release behavior is also different to that observed for the EHVE-containing formulations. However, given the lower costs of vinyl ether monomers, these data indicate that both DDVE and EHVE may be used in conjunction with UV9400 as cost-performance modifiers without greatly affecting release behavior.

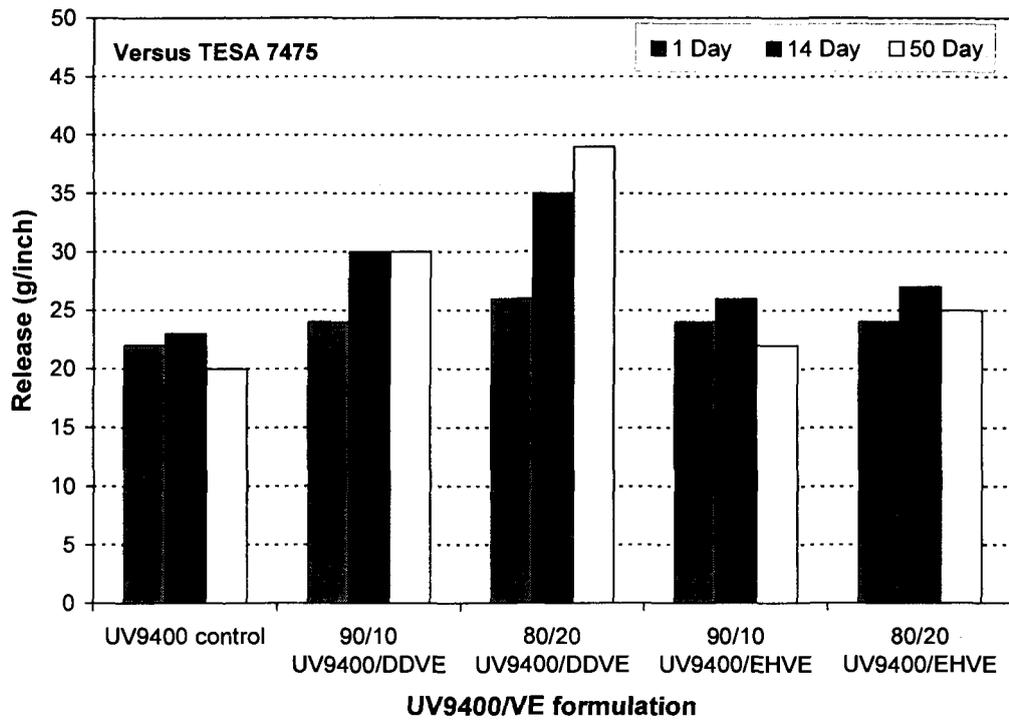


Figure 4. Release behavior of various UV9400/VE formulations measured (in g/inch; using a 1-inch wide tape) against TESA 7475 tape.

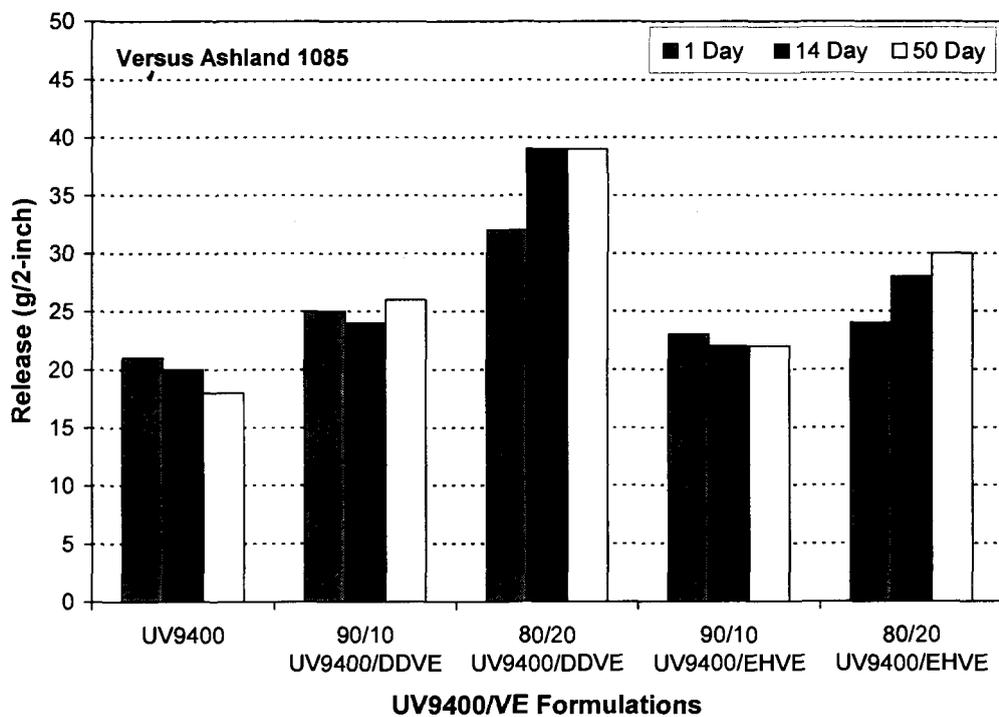
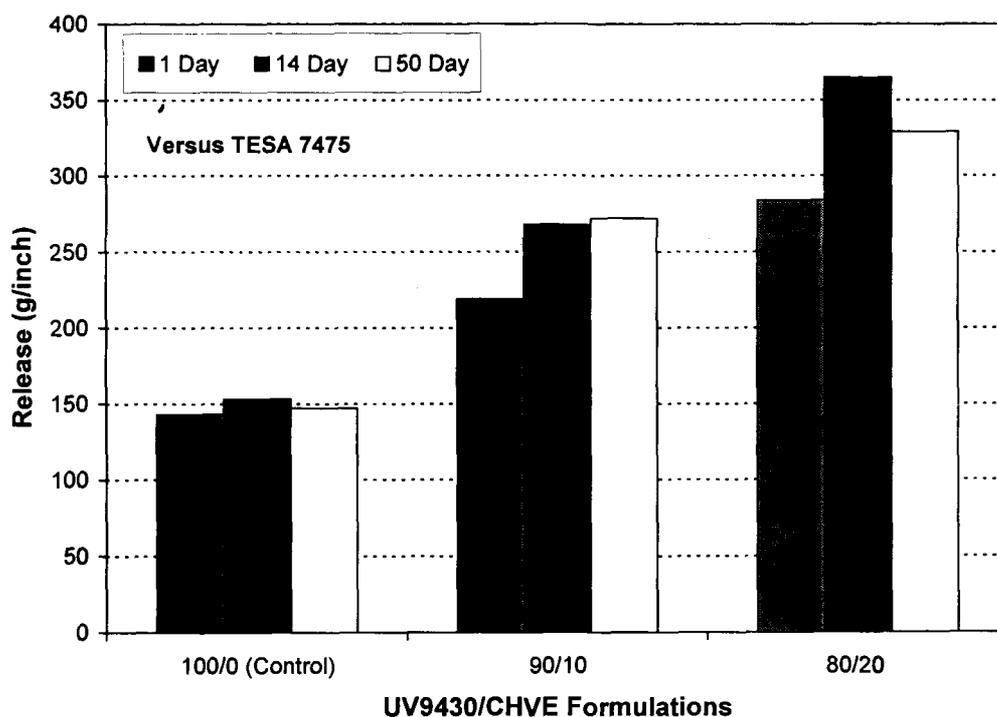


Figure 5. Release results for various UV9400/VE formulations measured (in g/2-inch; using a 2-inch wide tape) against the Ashland 1085 adhesive tape.

### Vinylethers as Controlled Release Additives

Data presented in Figures 6 and 7 show the increase in release, measured against the TESA 7475 and Ashland 1085 tapes respectively, observed by the addition of CHVE to formulations based on UV9430. In general, it is most desirable for release to remain stable throughout the shelf life of a tape or label, or to quickly move to a stable value. Release values less than 40 g/inch versus TESA 7475, or less than 30 g/2-inch versus ASHLAND 1085 acrylic PSA are considered low (or premium) release. Release values greater than 100 g/inch or 200 g/2-inch versus TESA and Ashland, respectively, are considered tight or 'controlled'. Several trends can be observed in this set of data presented in Figures 6 and 7. First, CHVE has a marked effect on the release behavior of the UV9430 tight-release polymer, particularly versus the Ashland 1085 adhesive (Figure 7). Second, when present in a release coating, CHVE makes aged release considerably less stable and release tends to rise on aging before leveling off after 7 weeks of aging (Figure 6). In the case of the release measured against the Ashland 1085 tape, this aging behavior appears more highlighted indicating a dependence on the type of adhesive used in conjunction with these systems. However, in both cases CHVE provides much greater 'CRA Effect' (Controlled Release Additive Effect) to the UV9430 coatings, which is of commercial significance.

Further investigations on the utility of EHVE as a low viscosity additive and CHVE as a controlled release additive, were performed on the 12 inch width Dixon coater at GE Silicones in Waterford, NY. These results are presented in Figure 8 and 9 and are based on medium release epoxysilicone UV9315 formulations cast on the Thilmany PK liner. In these runs, 2 parts of UV9380C were added to 100 parts of each UV9315/VE formulation. A target coating weight of 1.0 g/m<sup>2</sup> was accomplished using a 3 roll offset gravure coating station. Coatings were cured by exposure to one bank of 300 watt/inch Fusion Systems 'H' lamps at a line speed of 30 meter/minute, since the Dixon coater is not capable of faster speeds.



**Figure 6.** Controlled release behavior observed for various UV9430/CHVE formulations measured against the TESA 7475 tape (in g/inch).

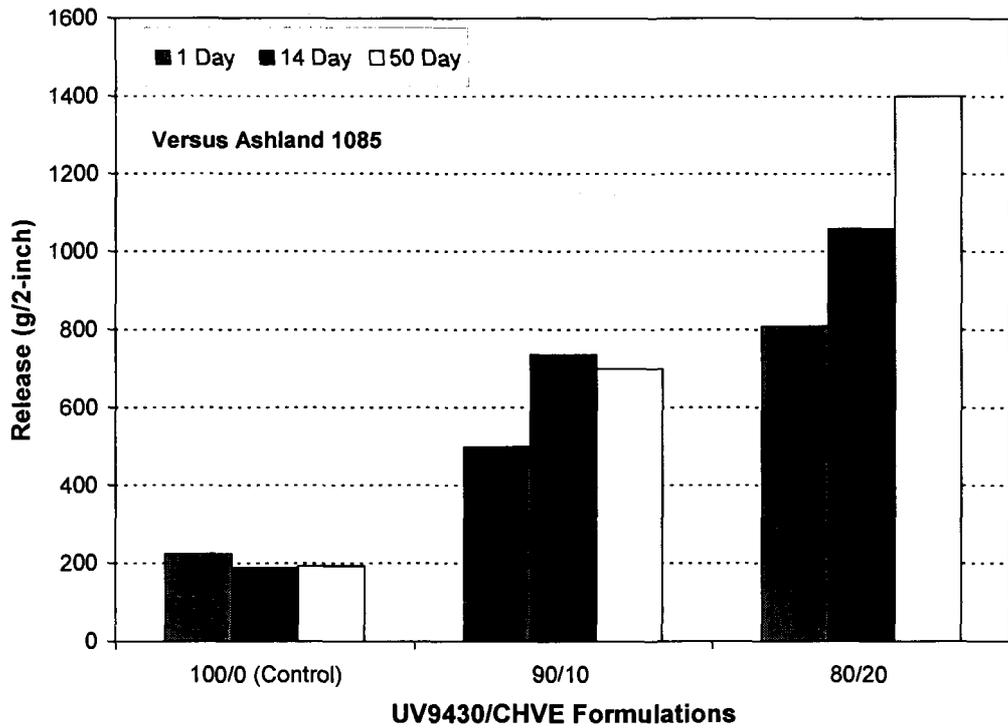


Figure 7. Controlled release behavior observed for UV9430/CHVE formulations measured against the Ashland 1085 tape (in g/2-inch).

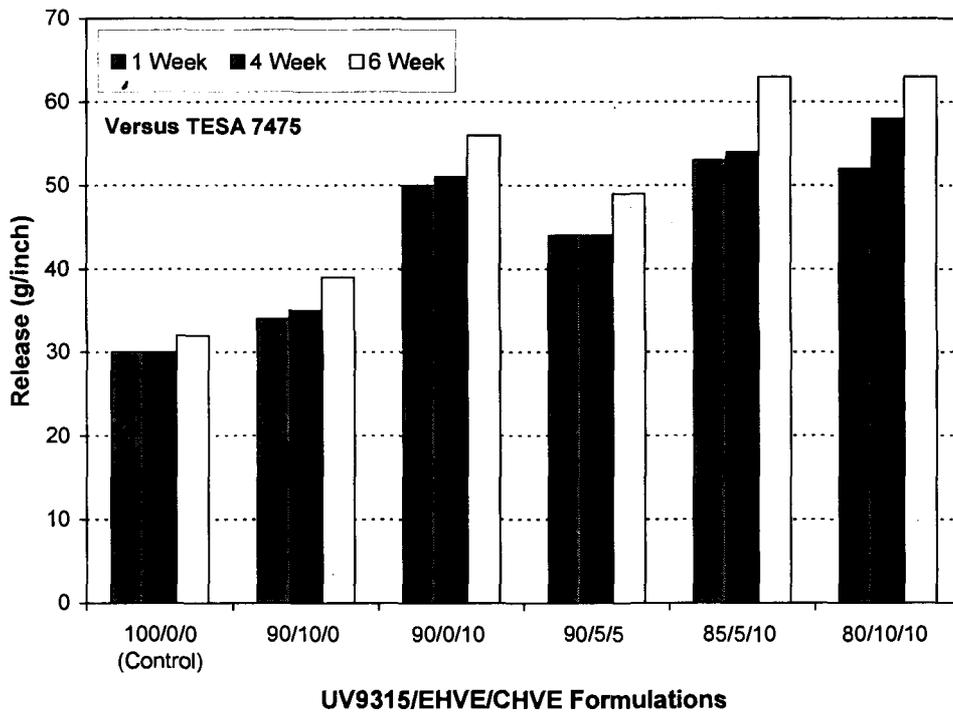
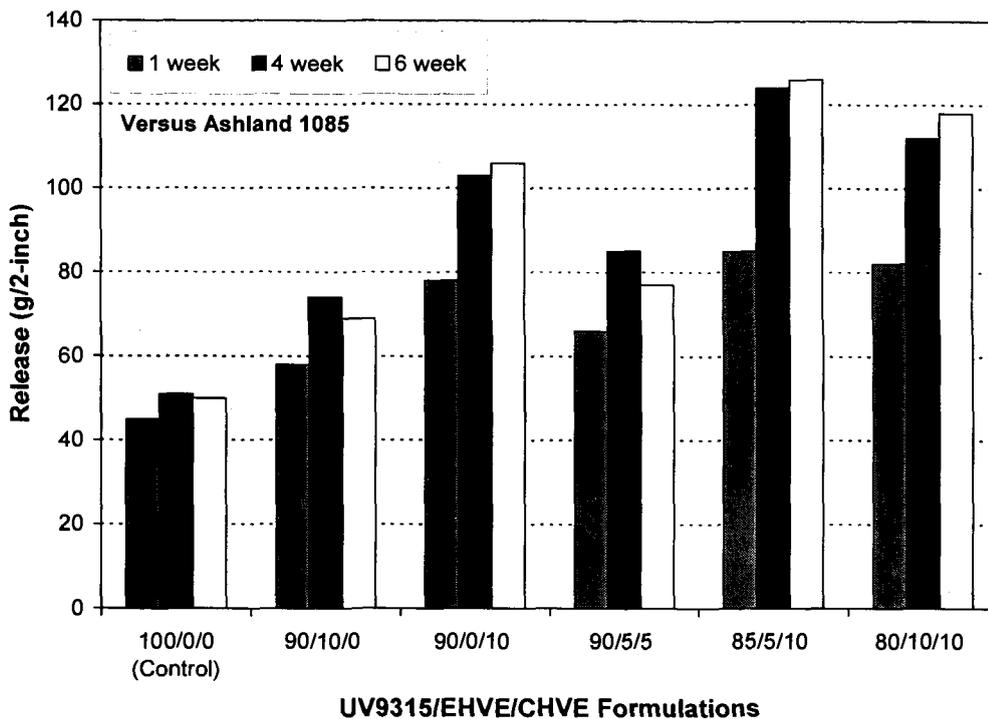


Figure 8. Release behavior measured (in g/inch) against TESA 7475 tape for formulations using EHVE and CHVE as additives to UV9315.



**Figure 9.** Release behavior measured (in g/inch) against Ashland 1085 adhesive tape for formulations containing EHVE and CHVE as additives to UV9315.

These data suggest that even low levels of EHVE when used with UV9315 increase the release marginally when evaluated against both adhesive tapes. The CHVE level in coatings based on the medium-release polymer UV9315 determines release differentials compared with the control (0 wt.% VE) coating. In addition, there is variation in aged release behavior depending on the type adhesive. Whether added alone or in concert with EHVE, in these experiments the CHVE level has a significant impact on release regardless of tape or adhesive against which the coatings were evaluated. Hence, CHVE can be used as a CRA to obtain modest release differentials. In order to investigate the effect of adhesive type on release behavior performance of these formulations was also evaluated against the TESA 4651 SBR-type adhesive tape. The results obtained are shown below in Table II. In this case the level of release is observed to decrease as the coating is aged. This result is interesting and may be either be attributed to minimal interaction between the adhesive and the release coating or the preferential migration of the epoxysilicone to the surface over time.

**Table II.** Release behavior of various UV9315/EHVE/CHVE formulations evaluated against the SBR-based TESA 4651 adhesive tape.

Formulation	Aged Release (g/inch)		
	1 Week	4 Week	6 Week
UV9315 Control	33	28	18
90/10 UV9315/EHVE	36	35	22
90/10 UV9315/CHVE	73	46	36
80/10/10 UV9315/EHVE/CHVE	77	46	34
85/5/10 UV9315/EHVE/CHVE	82	46	36
90/5/5 UV9315/EHVE/CHVE	53	35	23

Results obtained at ISP confirmed the utility of CHVE as a controlled release additive.<sup>6,14</sup> These studies evaluated various ratios of CHVE in a typical GE epoxy silicone resin (UV9300). Each formulation was found to be completely tack-free at our maximum conveyor speed of 600 fpm (75 mJ/cm<sup>2</sup>, AETEK). Incorporating 30 wt% CHVE was found to increase the release by a factor of three while improving the subsequent adhesion. Aging was found to have only a minor effect on release. Dougherty *et al* have reported similar results using the epoxy silicone (PC-600) and photoinitiator (PC-702) supplied by Rhodia.<sup>14</sup>

Epoxysilicone Formulations with High Vinylether Content

Shown in Figure 10 is the release behavior of various epoxysilicone/VE formulations containing up to 60 wt.% vinylether, evaluated against three different adhesives. While the release behavior was found to be a function of the type of adhesive tape used for evaluation, there are distinct advantages in terms of lower formulation viscosity. Compared with the high viscosity of the UV9425 (4000 cSt), the viscosity of the UV9425/UV9500/EHVE 40/0/60 mix was found to be 62 cSt, while the 40/10/50 blend exhibited a viscosity of 100 cSt. Further, the release performance and stability of the silicone coatings based on the high-viscosity UV9425 and 40-50% EHVE is remarkable, considering that the coating only partially contains PDMS. These coatings were extremely smooth and defect-free probably due to their low viscosity compared with most of the other coatings studied. We anticipate that such formulations will be of greatest commercial interest due to the cost-performance benefits offered to the end-user.

Studies conducted at ISP have also found that “premium” performance can also be obtained in vinylether formulations containing very low levels of epoxy silicones. For example, cured formulations cast on a PET substrate and based on DDVE crosslinked with small amounts of CHVE, modified with only 10 wt% UV9300 have an excellent combination of release and subsequent adhesion (Figure 11). This result is particularly significant considering the higher cost of epoxy functional silicones relative to vinylethers.

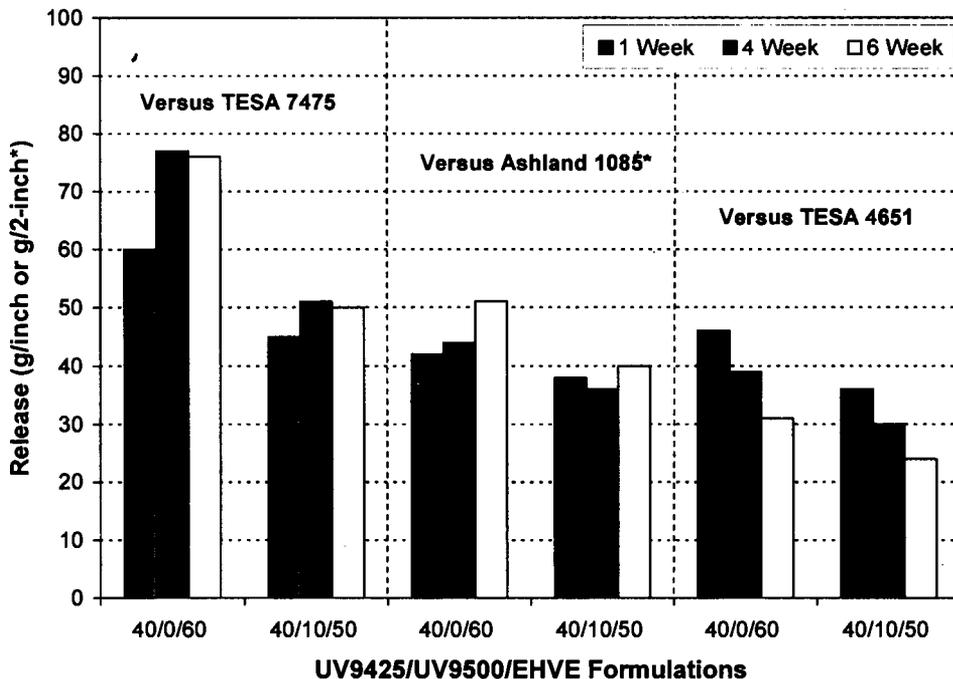
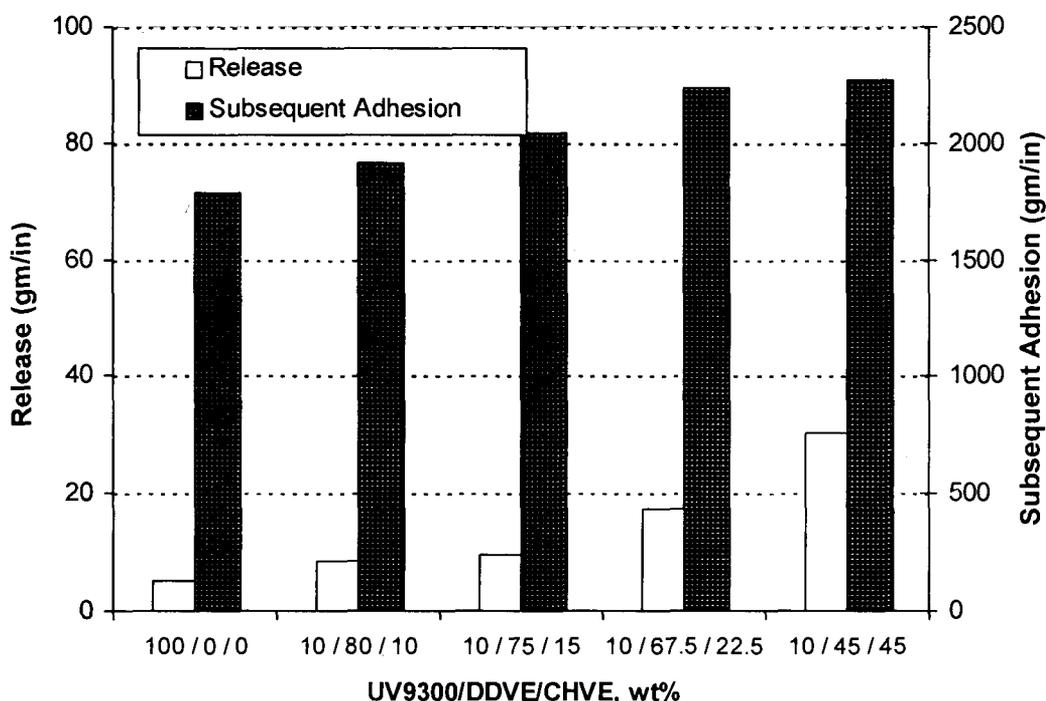


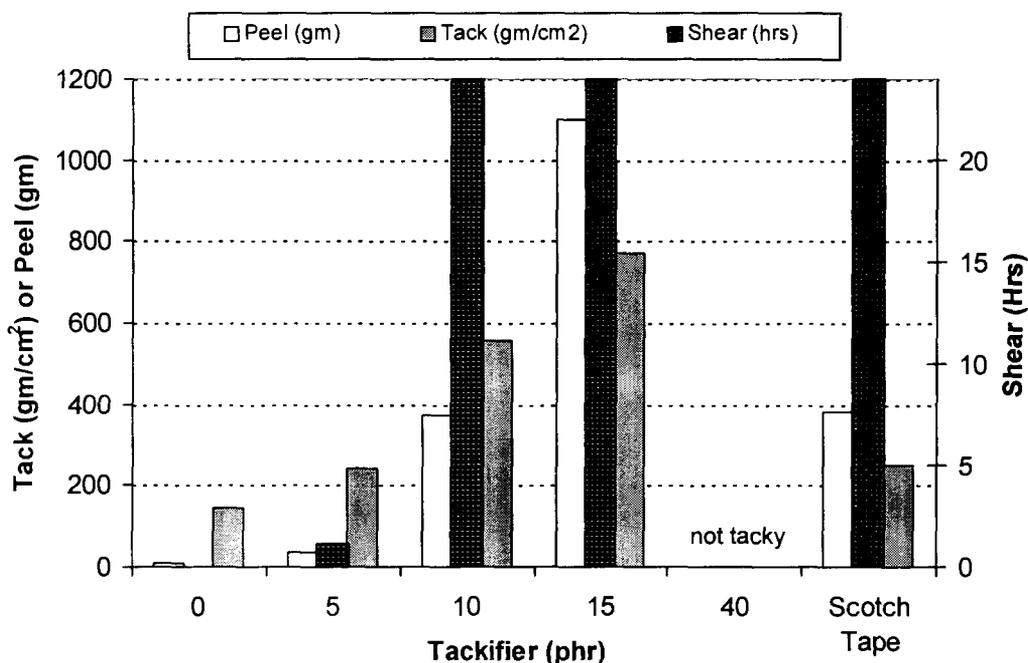
Figure 10. Release behavior of formulations based on UV9425/UV9500 with high EHVE content, evaluated against three different types of adhesive tapes.



**Figure 11.** Release and subsequent adhesion measured versus TESA 7475 tape for UV9300/DDVE/CHVE blends containing 3 phr photoinitiator (UV9380C), cured in air at 60 fpm (270 mJ/cm<sup>2</sup>, Fusion)

### UV-Curable Pressure Sensitive Adhesives (PSAs)

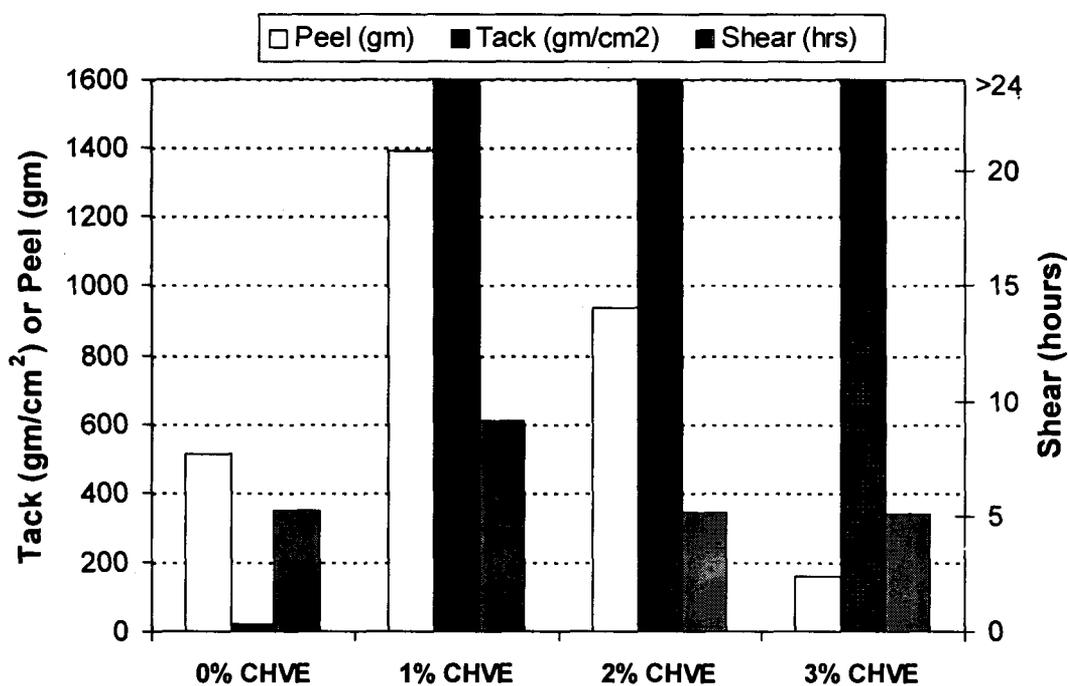
We had earlier reported that EHVE (low T<sub>g</sub> monomer) copolymerized with CVE (high T<sub>g</sub> monomer) and varying amounts of DVE-3 (crosslinker) provided an adhesive with a high degree of tack but poor peel and shear strength.<sup>15</sup> It was also suggested that incorporation of a tackifying resin should improve performance. We have found that a good balance of tack, peel and shear can in fact be obtained in vinyl ether systems by the addition of a suitable tackifying resin. Excellent results were obtained using a hydrocarbon resin (Regalrez<sup>®</sup> 1085, Hercules). For example, EHVE crosslinked with 1 wt.% CHVE in the absence of a tackifier cures rapidly to form a tacky mass with essentially no peel or shear strength. Incorporating 5 to 15 phr (parts per hundred resin) Regalrez<sup>®</sup> 1085 increases both peel and shear strength while lowering formulation cost. Very high levels of resin (40 phr) eventually degrade performance. At 10-15 phr tackifier, performance is equal to or superior to a commercial tape (Figure 12). Patent literature has shown that vinyl ether based UV curable PSA's can be prepared by copolymerizing a low T<sub>g</sub> and a high T<sub>g</sub> vinyl ether in the presence of a cationic photoinitiator, crosslinker, and tackifying resin.<sup>16</sup> Our results demonstrate that acceptable performance may be achieved without the inclusion of the high T<sub>g</sub> monomer in UV-curable PSA formulations containing vinyl ethers.



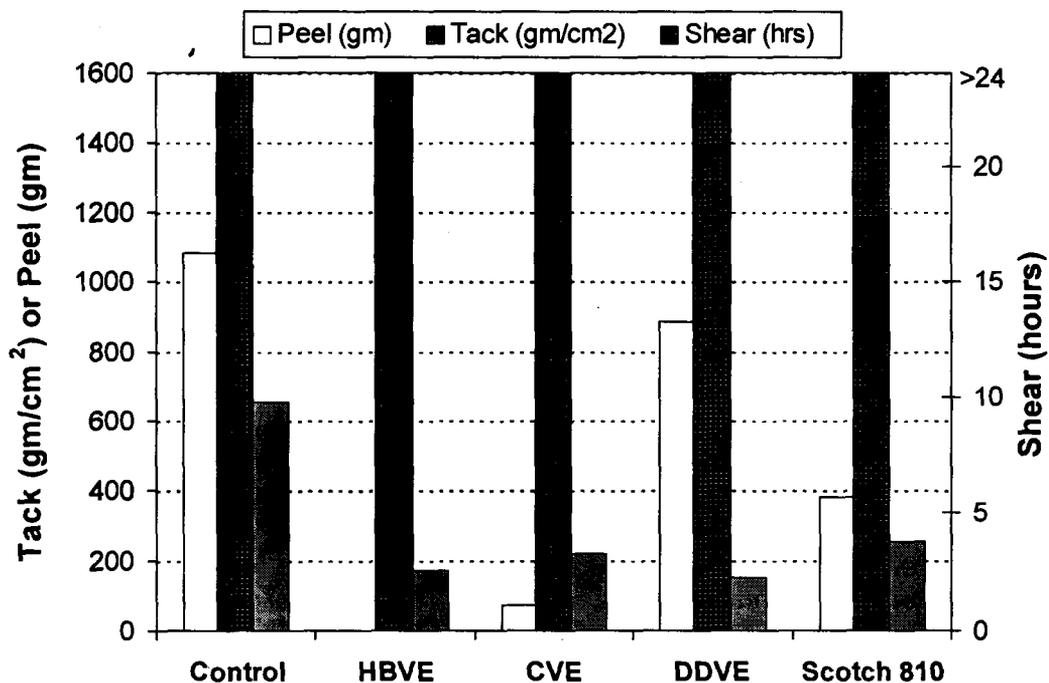
**Figure 12.** Effect of amount of tackifier of the adhesive properties of a formulation containing 99% EHVE/1% CHVE and 2 phr UV9380C cationic photoinitiator.

Based on the data in Figure 12, the formulation containing 15 phr tackifier was chosen for further evaluation. To determine if the PSA exhibits good adhesive consistency over the entire length of the test area, the Gardner Slip/Peel Tester was equipped with a computer data collection system to create a plot of peel strength as a function of time. Results demonstrated good adhesive consistency over the entire length of the test area. Peel consistency is comparable to the commercial tape with the advantage of improved peel strength. Plotting peel versus time is also an excellent way to demonstrate the effect of post cure. Note that all the PSA's evaluated above were tested after a thermal post treatment (70°C for a minimum of 15 min). It was observed that during the post cure, peel strength improved dramatically, therefore all samples were post cured as standard procedure. While epoxy formulations are well known to exhibit a pronounced post cure, it was interesting to observe a demonstrable post cure in 100% vinyl ether formulations.

*Effect of Type and Amount of Crosslinker and Comonomer.* The performance of DVE-3 and CHVE as crosslinkers was compared at a constant tackifier level (15 phr). Both formulations exhibited good tack, and as expected, in the absence of any crosslinker, these compositions have essentially no shear strength. It was observed that CHVE provided the highest shear strength while DVE-3 contributed to the highest peel. Also, at constant tackifier level (15 phr), increasing the level of crosslinker (CHVE) decreased tack and peel, while shear strength remained greater than 24 hours (Figure 13). To study the effect of comonomers, the performance of several monovinylethers was compared in the following prototype formulation: 25 wt% comonomer, 74 wt% EHVE, 1 wt % CHVE, 15 phr Regalrez 1085, 2 phr UV 9380C. The control formulation containing 99% EHVE provided the best combination of properties, while DDVE may be preferred as a comonomer in formulations where low tack is desired (Figure 14). These data demonstrate the ability of vinyl ether comonomers to impart the desired combination of peel, shear and tack to suit a particular application.



**Figure 13.** Effect of amount of crosslinker (CHVE) on a formulation containing EHVE, 15 phr tackifier and 2 phr UV9380C cationic photoinitiator.



**Figure 14.** Effect of inclusion of 25wt% comonomer on the adhesive properties of a (74wt%) EHVE/(1wt%)CHVE/(15phr)tackifier PSA formulation.

*Effect of Viscosity.* The formulations described so far were all very low in viscosity due to the high monomer content. For example, a composition based on 99 wt% EHVE containing 1 wt% CHVE and 15 phr Regalrez® 1085 is too low in viscosity (22 cps) for many application techniques. Increasing viscosity by adding additional tackifier degrades performance as described above. Viscosity can be readily adjusted by incorporating low levels of non-reactive fillers of which, poly(isobutylene) was found to be particularly effective (Table III).

**Table III.** Effect of a non-reactive filler on the formulation viscosity

<b>FORMULATION (grams)</b>	<b>A</b>	<b>B</b>	<b>C</b>
EHVE	99	99	99
CHVE	1	1	1
UV9380C	2	2	2
Regalrez 1085	15	15	15
Poly(isobutylene) level	0	2.5	7.5
Viscosity (cps)	22	64	475
Peel (gm/lin)	1391	1300	900
Tack (gm/cm <sup>2</sup> )	606	651	676
Shear (hrs)	> 168	> 168	> 168

## UV-Curable Laminating Adhesives

### Cationic Formulations

Cycloaliphatic epoxy adhesive formulations can be modified with vinyl ethers to result in laminating adhesive compositions with lower viscosity and reduced cure time. These formulations were evaluated for laminating glass (microscope slides) to glass, and glass to steel. As shown below, the lap strength of these laminates exceeded the strength of the glass; the glass fractured at an ultimate tensile strength between 225 and 360 psi leaving the adhesive joint intact. While the vinyl ether does not contribute to the strength of this bond it does significantly decrease fixture time and formulation viscosity (Table IV).

**Table IV.** Cationic laminating adhesive formulations containing vinyl ethers

<b>FORMULATION (grams)</b>	<b>A</b>	<b>B</b>
UVR-6110	100	80
CHVE	--	20
UVI-6990	3	3
Viscosity (cps)	580	150
Fixture time (glass/glass)	60 sec.	45 sec.
Fixture time (glass/steel)	>140 sec.	68 sec.
Lap shear (glass/glass)	229 psi*	260 psi*
Lap shear (glass/steel)	360 psi*	300 psi*

\* glass fracture

### Charge Transfer Formulations

Non-acrylate, charge transfer formulations can also be used as laminating adhesives. In this case, adhesion to glass and steel is generally not as good as the cationic formulations described above; however adhesion to plastic films is often excellent. For example, a charge-transfer DVE-3/unsaturated polyester formulation was used to prepare polyester film to polyester film lap joints. The strength of the joint exceeded the strength of the polyester substrate (Table V).

### Free Radical Formulations

Vinylethers are known to be effective reactive diluents for acrylate oligomers in free radical<sup>17</sup> and hybrid<sup>18</sup> formulations. While most of this work has been directed toward coatings, it would be interesting to extend this technique to adhesives. The performance of an acrylate monomer pentaerythritol tetraacrylate (PETA)/DVE-3 free-radical formulation was compared to the same formulation containing a cationic photoinitiator (FX-512) (Table VI). Polyester laminates were prepared and cured using the AETEC 1202 UV processor. In each case, the lap strength of polyester to polyester laminates exceeded the strength of the polyester. Our data suggests that the cationic photoinitiator is not required presumably due to the high ratio of acrylate to vinylether functionalities. A high acrylate to vinylether ratio helps ensure complete conversion of the vinylether double bonds.

Table V. Charge transfer laminating adhesives for polyester-to-polyester laminates

FORMULATION (grams)	D	E
Cargill UV Resin 15-1565	70.0	70.0
DVE-3	30.0	15.0
CVE	--	18.7
t-butyl hydroquinone (ppm)	500	500
Irgacure 184	3.0	3.0
Viscosity (cps)	4900	2000
Fixture time (sec.)	<0.1	0.3
Lap shear (psi)	101*	36
* substrate failure		

Table VI. Laminating adhesive formulations containing vinylethers for polyester-to-polyester laminates cured by free-radical (F) and hybrid (G) schemes

FORMULATION (grams)	F	G
PETA	80.0	80.0
DVE-3	20.0	20.0
DC-193 surfactant	0.3	0.3
Irgacure 184	3.0	3.0
FX-512	--	0.6
Viscosity (cps)	90	90
Fixture time (sec.)	<0.1	<0.1
Lap shear (psi)	111*	107*
* substrate failure		

## CONCLUSIONS

Vinylethers offer distinct viscosity-lowering and cost-performance advantages in the formulation of UV curable release coatings, pressure-sensitive adhesives (PSAs), and laminating adhesives. The effectiveness of vinylethers in lowering viscosity, imparting controlled release behavior, increasing cationic photoinitiator miscibility, and in contributing to lower costs and efficient release properties of formulations based on epoxy silicones was presented. Specifically, the addition of CHVE to epoxysilicone formulations was found to increase the level of release, while the addition of DDVE and EHVE lowered formulation cost and viscosity while maintaining release performance. Further, formulations that contained large amounts of vinylethers resulted a very low formulation viscosity and excellent cured-film release behavior. It was determined that the release properties may be readily controlled by appropriate selection of the type and amount of vinylether, as well as the crosslink density. The release behavior was also found to vary based on the adhesive tape against which the performance was measured.

UV-curable PSA compositions based primarily on mono- and bifunctional vinylethers demonstrated excellent adhesive characteristics with the addition of small amounts of a tackifier. The effect of varying the tackifier level and the nature and amount of bifunctional vinylether crosslinker on adhesive performance, was demonstrated. UV-curable laminating adhesive compositions based on cationic, free-radical, and hybrid chemistries, for glass-to-glass, glass-to-metal, and polyester-to-polyester lamination, were briefly discussed. It is, therefore, possible to formulate both UV-curable release coatings, as well as laminating and pressure sensitive adhesives using various vinylethers and additives to match specific release and adhesive requirements.

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