SHORT-CHAIN ORGANOSILICONE ADDITIVES for CATIONIC UV CURE COATINGS

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Introduction

A considerable body of work has been published that describes the use of alcohols, polyols, gycidyl ether and vinyl ether compounds, and, more recently, oxetane monomers, as reactive diluents and modifiers in cationic type radiation curable coating formulations (1-4). Details of the effects of compatible vinyl ether and oxetane compounds on the performance of photocurable epoxysilicone release agents have been presented at industry forums and taught in the patent literature (2, 5). While the efficacy of such additives for release applications has been well demonstrated, commercial practice of adding non-silicone modifiers to UV cure epoxysilicone release coatings has been limited due to price and availability of many materials, and to some undesirable performance features inherent in their use. We therefore undertook a study of low molecular weight 'short-chain' epoxyfunctional silicone polymers as viscosity-reducing agents and additives for conventional epoxysilicone release coatings. In the course of this work we found that certain reactive telechelic short-chain silicone polymers are compatible with non-silicone photocurable compounds. Reactive 'short-chain' silicones are novel additives that provide silicone properties of slip and release in compatible UV curable non-silicone formulations. We herein define 'short-chain' as < 50 linear dimethyl siloxane units.   Details of this program are provided in the balance of this presentation.

Experimental

Commercial epoxysilicone polymers, vinyl ether monomers, and other readily available coating materials were obtained from their vendors and used as furnished. Since most of these products' compositions are well known to experienced formulators they are identified by their commercial names, when appropriate, for sake of convenience. *Use of commercial product designations does not imply any endorsement or recommendation for their use, and does not constitute a sales presentation.* Release coating trials were carried out on the 18 inch pilot coating line at Black Clawson Converting Equipment, Inc., in Fulton, NY, with cure effected by exposure to one or two banks of Fusion Systems[TM] H lamps operating at 400 or 600 watt/in nominal UV power, and on the 12 inch pilot coating line at GE Silicones Technology Dept, Waterford NY, with cure effected by exposure to one Fusion Systems H lamp operating at 300 watt/in power. Lab draw down experiments of various coatings were conducted by manual blade-applied neat material or Meyer-rod coating of solvent-borne formulations, cure being effected by exposure to a single 200 watt/inch Hanovia medium pressure mercury vapor arc lamp mounted in an RPC Lab QC1202 Processor. Release testing utilized a ZPE1000 High speed release tester (Instrumentors Co) or a TMI release test instrument for low speed peel release measurements. Coefficient of Friction results were compiled using an Instrumentors[TM] Slip/Peel Adhesion Tester. Brookfield LVF viscometers and Ostwald tubes were used for viscosity determination. Details of other experimental procedures, syntheses, and etc. will be reported below.

'Short Chain' Polysiloxanes

Conventional photocurable cycloaliphatic epoxy functional linear polydimethylsiloxanes (PDMS) are usually applied solvent-free using sophisticated multi-roll film-splitting or 3 roll offset gravure coaters capable of high speed defect-free deposition of 0.5 – 2.0 gram/meter^2 weight of silicone onto film or paper substrate. These polymers were designed to mimic the coating rheology and hold-out characteristics of existing solvent-free thermal cure silicone release agents, and are therefore of molecular weight providing 200 – 600 cstk viscosity. Silicone polymer structure is conveniently represented by means of a 'shorthand' nomenclature: commercial epoxysilicone polymers can be depicted in this fashion:

$$\mathbf{M^E\ D_x\ D^E{}_y\ M^E} \quad \text{or} \quad \mathbf{M\ D_x\ D^E{}_y\ M}$$

'E' refers to the cyclohexylepoxy-ethyl- group and lack of a superscript denotes methyl substituents on 4-coordinate silicon atoms. 'M^E' indicates this structure
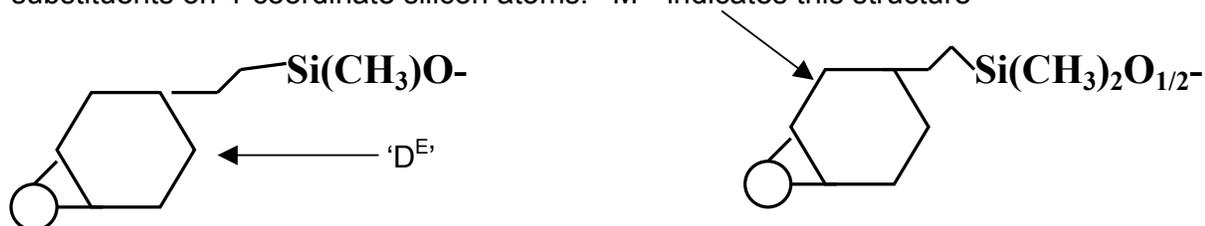

The sum of (x + y) in conventional epoxysilicone coatings is ~ 75 to 150, with x/y usually > 4. Unless otherwise noted, this convention implies random situation of 'D' groups.   Commercial production of these polymers is well established, with the epoxy group derived from hydrosilation addition of 4-vinylcyclohexenoxide (VCHO) to preformed SiH- functional precursor silicones (6). Photocure of coated epoxysilicones requires the presence of compatible iodonium catalysts designed for use in nonpolar silicone media, as previously described (7, 8).   Crosslinked (cured) epoxysilicones can be represented as poly(cyclohexyloxide) with pendant PDMS attached, as shown in *Figure 1*.

Low viscosity photocurable silicone coating formulations are useful for application on transparent films where low coatweight is applied to retain the optical clarity of the film after silicone has been coated and cured on it. Reduced viscosity is also useful on coating lines lacking the expensive coating equipment designed to handle conventional solvent-free silicone release agents. Direct gravure or flexo coating technique are often used on narrow web UV presses; these methods are well suited for low viscosity coating materials. Since radiation cure silicones are mostly applied to film (plastic) substrate, viscosity designed for silicone coating on porous paper is not needed.   Coating from dilute solution in volatile solvents is often practiced to achieve low coatweight or to overcome equipment limitations, but converters using solvent vehicles have to contend with hazardous chemical handling and disposal, and with environmental regulation that adds cost and complexity to their operations. Design of a low-viscosity epoxysilicone polymer for use as a viscosity modifying additive in UV curable release coatings drew upon results of previous studies in these and other

laboratories, some of which have been published (9). Epoxy content, polymer structure, and, of course, polymer molecular weight are controllable and can be easily varied.

Figure 1
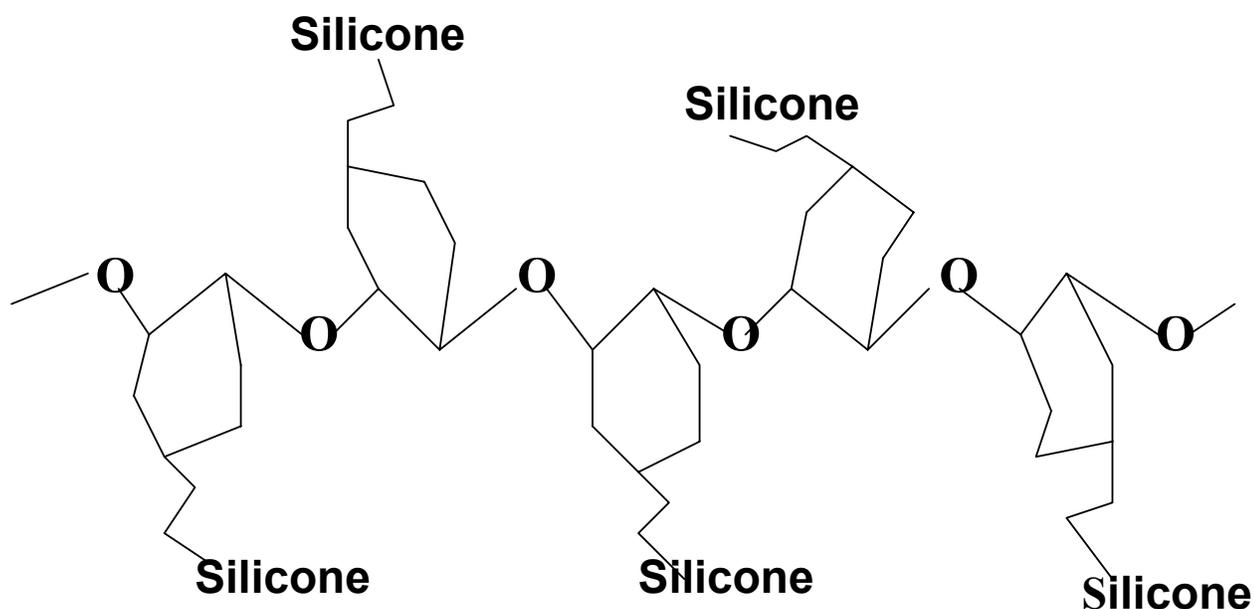
After preliminary work with $MD_xD^E_yM$ and $M^ED_zM^E$ polymers, where x + y ~ z < 100, we decided that a telechelic structure, that is, linear PDMS with reactive epoxy groups at the chain end positions, was the most promising model molecule for a release coating additive. Earlier work had established that such structures where z>50 were slow to cure and not very miscible with commercial iodonium SbF_6 photocatalysts (9). Accordingly, a series of linear epoxy-stopped PDMS molecules with z ~50 or less was synthesized and viscosities measured (following vacuum removal of excess VCHO and cyclic non-reactive siloxanes), with results noted in *Table 1.*

Table 1: Linear Epoxy-stopped Siloxanes $M^ED_zM^E$

Z	Viscosity (Ostwald), cstk	Epoxy Equiv. Wt.
0	30	191
3.5	19	321
7.5	25	468
10	34	561
22	52	1005
50	90	2041

The anomalous viscosity for z=0 disiloxane may have resulted from some polymerization of the very reactive molecule during processing.

Cationic photocatalysts developed for commercial use with epoxysilicone polymers include a class of bis(4-alkyl)phenyl iodonium hexafluoroantimonate (DDISbF6) derived from 'linear alkylate' grade dodecylbenzene (10, 11). Based on the normal alkylbenzene mix, the active iodonium salt is a mixture of over 100 discrete compounds and not a pure substance; its miscibility in nonpolar polymers is sufficient for it to be useful for photocure of epoxysilicone release agents and well-suited for photocurable non-silicone cationic coatings. A commercial product, UV9390C (a solution of DDISbF6 in an alkyl glycidyl ether diluent plus thioxanthone sensitizer), was completely soluble in the $M^E D_z M^E$ series where z <25, and was partially soluble to a stable suspension where z = 25-50. Since reactive linear silicone polymers with epoxy only at termination sites cannot crosslink in the fashion of multifunctional epoxysilicones, 'curing' of these materials by exposure to UV light in the presence of compatible iodonium catalysts occurs by rapid chain extension. We found that linear epoxydimethylsiloxy-stopped short chain polymers where z = 0 – 25 very efficiently cured to migration free materials when mixed with 1 or 2 phr UV9390C, applied to film substrates (including PET, PE, and PP) as a thin (~ 1 micron) coating and exposed to focused medium pressure mercury vapor lamps. UV flux of 20 to 40 mJ/cm^2 was sufficient to produce well-cured coatings. By contrast, the epoxy-stopped linear polymer where z = 50 required ~ 100 mJ/cm^2 focused UV radiation to convert to a migration free abhesive coating under identical conditions of photocatalyst concentration, substrate, and coating thickness. As these polymers were developed for use as additives in UV cure epoxysilicone release coatings, it was useful to then determine if they would act as release coatings upon cure. Accordingly, 25% solutions of $M^E D_z M^E$ where z = 0, 3, 7.5, 10, 22 and 50 were made up in methylene chloride, 2 phr of UV9390C catalyst solution (as a function of the epoxysilicone polymer) added, the solution applied to 1.5 mil PET film using a lab coater equipped with a # 5 Meyer rod, then cured by exposure to ~ 100 mJ/cm^2 UV flux in the RPC Processor. TESA 7475 acrylic test tapes were applied to the cured silicone coatings, and release tested at 300 ipm on the ZPE1000 device after 2 weeks' aging at ambient conditions. Results are displayed in *Table 2* below.

### Table 2: Release from $M^E D_z M^E$ silicone coatings

Z	TESA 7475
0	No release
3	55.0 g/in (very 'zippy', uneven peel)
7.5	23.0 g/in (slightly 'zippy', initiation spike observed)
10	20.7 g/in (slightly 'zippy')
22	11.6 g/in (smooth peel)
50	12.4 g/in (smooth peel)

The $M^E D_{22} M^E$ polymer (designated Polymer 1193 for no particular reason) provided the best combination of viscosity reduction, good iodonium catalyst compatibility, and useful release properties.
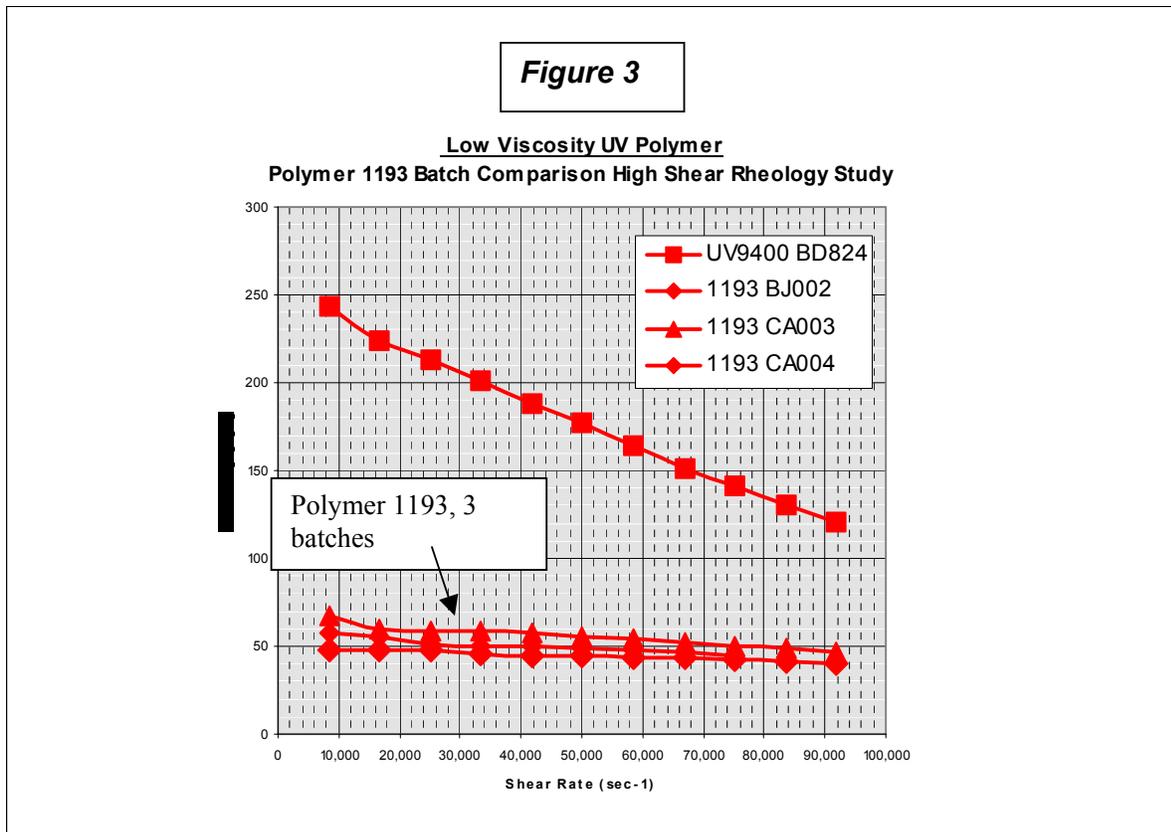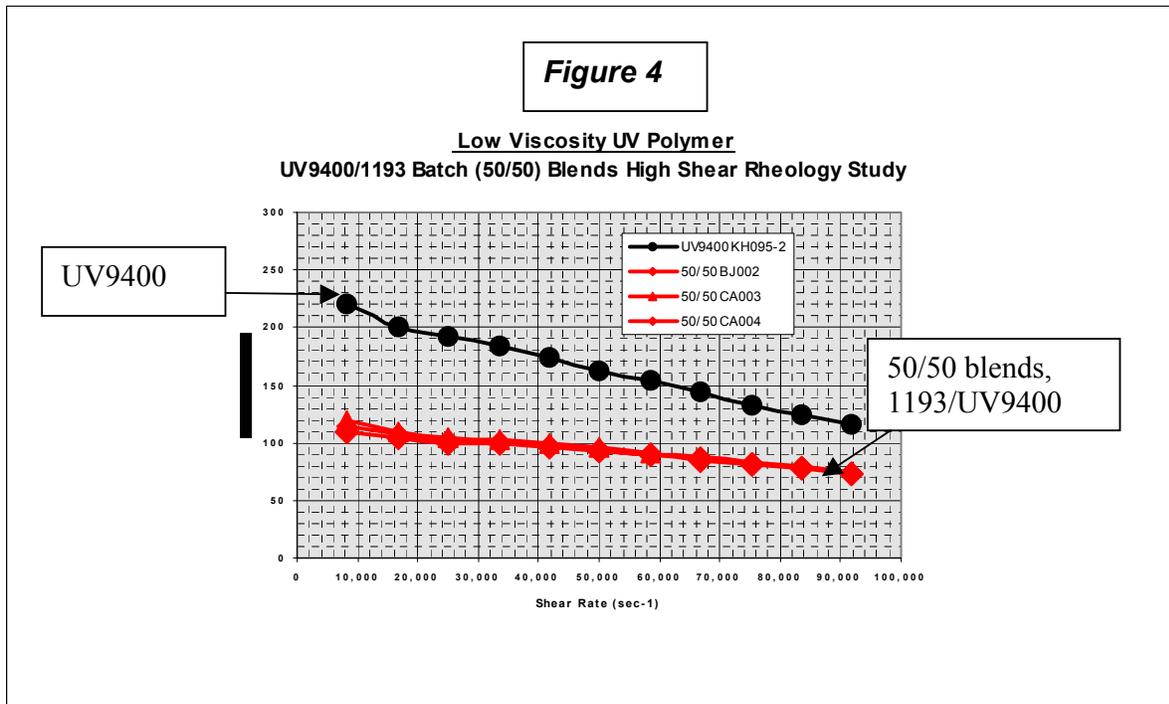
Release Coatings with Candidate Polymer Additive

Blends of polymer 1193 with a commercial epoxysilicone were prepared to determine its efficacy as a viscosity reducing agent. Results are displayed in **Figure 2**
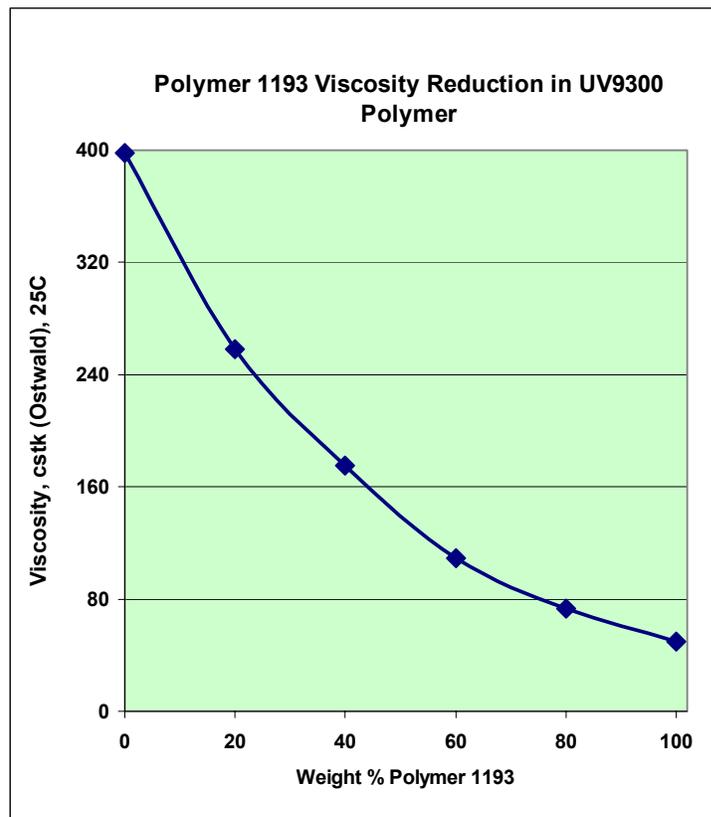
Polymer 1193 is an effective diluent when blended with commercial epoxysilicone polymers: a 25% mix with UV9300 in this experiment cut the blend viscosity in half. Static viscosity measurements, such as the Ostwald tube determination, are useful but do not provide prediction of polymer coating behavior over wide variation in shear conditions encountered on production coating equipment, particularly multiroll coaters. Accordingly, the viscosity behavior of Polymer 1193 as a stand-alone polymer and in blends with a commercial epoxysilicone was analyzed under high-speed shear conditions. Mixes of 1193 with UV9400 polymer (a linear multifunctional epoxysilicone) were prepared and their viscosity determined at a range of shear conditions, using a Haake[TM] High Shear Viscometer. Conventional
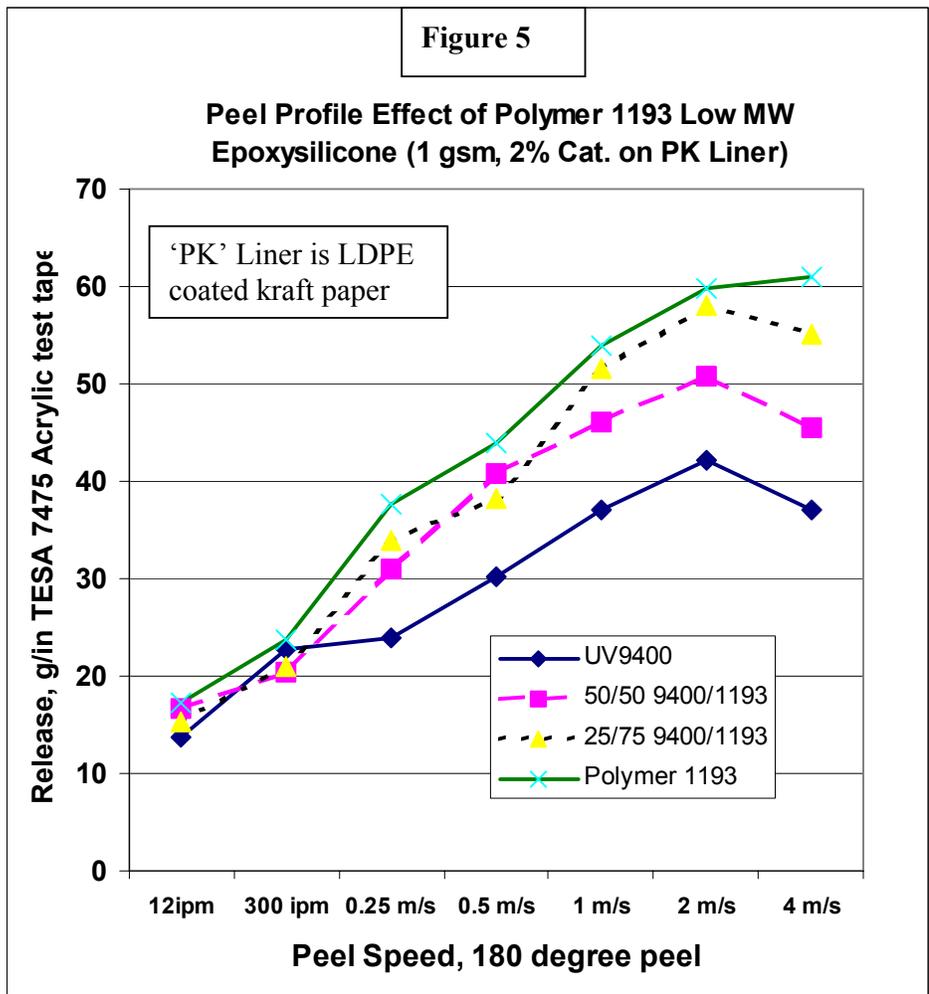
multifunctional epoxysilicone polymers undergo significant shear thinning, so it was of interest to find out if the epoxy-chainstopped Polymer 1193 would behave the same way. Results of this determination are displayed in *Figures 3 and 4* below.

Figure 3

Low Viscosity UV Polymer
Polymer 1193 Batch Comparison High Shear Rheology Study

Polymer 1193, 3 batches

Legend:
- UV9400 BD824
- 1193 BJ002
- 1193 CA003
- 1193 CA004

X-axis: Shear Rate (sec-1)

Figure 4

Low Viscosity UV Polymer
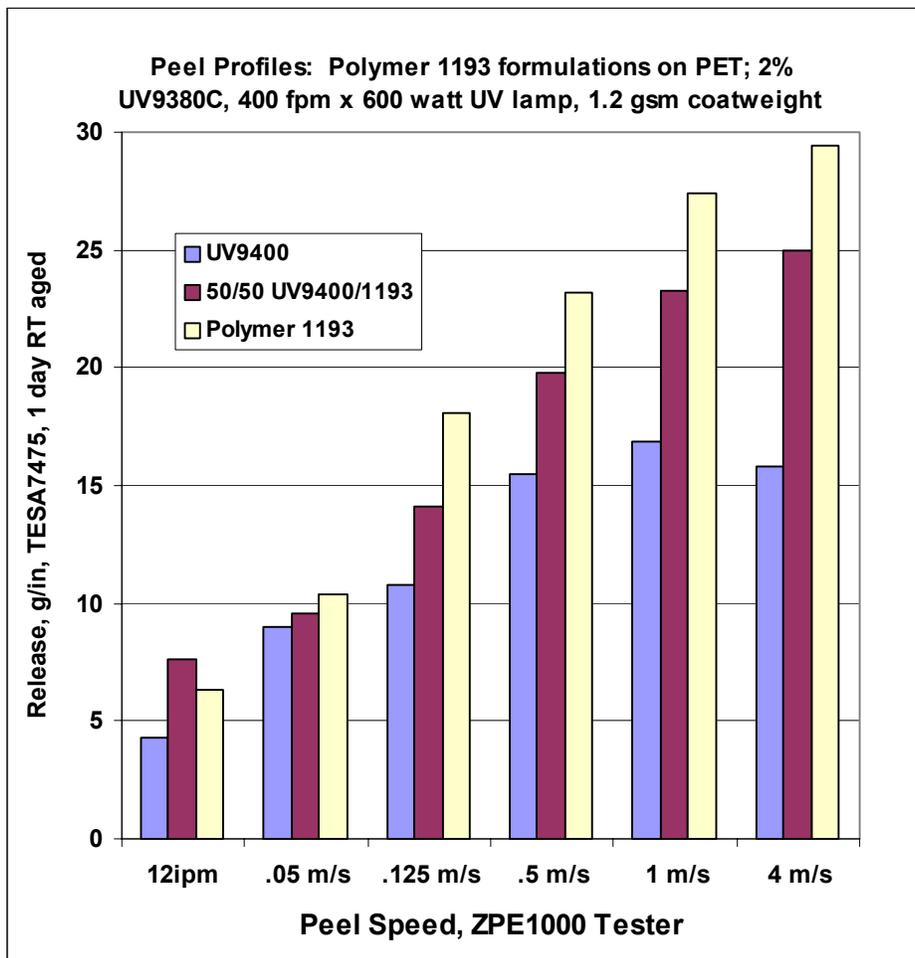**UV9400/1193 Batch (50/50) Blends High Shear Rheology Study**

The results showed that Polymer 1193 displays little shear-thinning, and that its presence in blends with conventional epoxysilicones reduces shear-thinning as well. The additive provides for a more Newtonian coating formulation that simplifies high speed coating operation in that coating rheology does not show much variation as a function of line speed.

Polymer 1193 was tested in release coating formulations by running numerous trials of the additive with commercial epoxysilicone release polymers on the pilot coater at Black Clawson Company. A 5 roll film splitting coater was used, running at 400 – 1200 fpm with UV lamp power varied between 400 watt/in and 1200 watt/in. Several film substrates, including polyethylene kraft (PK), HDPE, and PET were coated. Excellent cure to non-smear and non-migration coatings was recorded over a 9-fold range of UV flux for all coatings tested, although it should be noted that rapid cure of commercial epoxysilicone release coatings is largely dependent on substrate compatibility with cationic cure chemistry, and that substrates used were known to be a good match with UV epoxysilicone coatings. Cured coatings were laminated with TESA test tapes offline, and release of the silicone coated liner from the tapes was recorded as a function of ambient and oven aging. Peel release profile (release as a function of peel speed) of a typical series of trials of Polymer 1193 on PK liner is shown in **Figure 5.**

Figure 5

Peel Profile Effect of Polymer 1193 Low MW Epoxysilicone (1 gsm, 2% Cat. on PK Liner)

'PK' Liner is LDPE coated kraft paper

Legend:
- UV9400
- 50/50 9400/1193
- 25/75 9400/1193
- Polymer 1193

Y-axis: Release, g/in TESA 7475 Acrylic test tape

X-axis: Peel Speed, 180 degree peel (12ipm, 300 ipm, 0.25 m/s, 0.5 m/s, 1 m/s, 2 m/s, 4 m/s)

Release profile of blends coated on a 1.5 mil PET liner is displayed in *Figure 6*

Figure 6

Peel Profiles: Polymer 1193 formulations on PET; 2% UV9380C, 400 fpm x 600 watt UV lamp, 1.2 gsm coatweight

Peel Release Profile is considered 'flat' if release levels off or diminishes at high strip speed, and is termed 'dynamic' if release climbs as strip speed increases. Highly functionalized radiation curable silicone release coatings give rise to highly crosslinked, high modulus coatings characterized by flat peel profiles (subject to considerable variation due to substrate and adhesive) such as that of the commercial coating included in *Figures 5 & 6*. Given that the epoxy content of Polymer 1193 is greater than that of the commercial polymer UV9400, the dynamic peel release profile obtained in the above experiment was surprising. Polymerization by chain extension of the $M^E D_z M^E$ polymer apparently gives rise to a lower modulus coating than obtained from an $M^E D_X D^E{}_y M^E$ crosslinking polymer, despite the distance between crosslink sites on the latter molecule being greater than the chainlength of the epoxy-stopped PDMS molecule. Important applications of UV cured silicone release agents on film liners include 'no label look' clear labels mechanically applied to jars and bottles, particularly cosmetic containers. Automatic dispensing of die-cut labels from the liner to the package is a high-speed operation requiring that labels not be dislodged from liner until being picked off and stuck on the article…if high speed release is too easy, 'premature dispensing' occurs and labels fly off the liner ahead of the application station. A dynamic peel profile is therefore highly desirable for these products, as this performance helps insure that labels stay put on the liner until point of release.

Novel One Part UV Cure Epoxysilicone Coatings

While the converting industry undergoes mergers and acquisitions, and companies exit this highly competitive arena, there has been growth of so-called narrow web coaters making profitable specialty converted products in small lots to serve niche customers. Narrow web operations use inks, topcoats, and other coatings that are usually printed on flexible substrates. Many narrow web presses cure all formulations with UV, and most of the products used on this equipment are convenient one-part, off-the-shelf materials. UV cure silicones are part of this product mix, and one-part UV silicone formulations are highly desirable. Efforts to design viable one-part UV silicone release coatings that include the bis(alkylphenyl) iodonium SbF_6 photocatalyst have been reported (12). Such formulations lack shelf stability because effective concentrations of this photocatalyst promote rapid, unpredictable crosslinking of conventional multifunctional epoxysilicone polymers after a few days' or weeks' dark storage. Given the low viscosity of Polymer 1193 and its lack of reactive sites along its polymer chain, it was reasonable to consider using the new 'additive' polymer as the *base polymer* for a one-part UV cure silicone package.

In order to provide for optimal release performance without introducing crosslinkable reactive polymers into candidate one-part UV release packages, a commercial long-chain (over 100 'D' units) silicone polymer with di(carbinol) reactive functionality in chain-stopper positions, described in recent presentations and patents (13, 14), was included with Polymer 1193 in experimental designs. This product is designated Polymer A in this paper. It was important that candidate one-part UV release formulations be homogeneous solutions of polymers and DDI-SbF_6 lest catalyst be lost on standing, so low levels of alkylphenol were also part of the blends. The photocatalyst solution chosen for this study was a commercial product, UV9385C, similar to UV9390C but without sensitizer; it was felt that eliminating thioxanthone from the product would make the product less prone to gelling on exposure to ambient light on a press. Candidate formulations are shown in *Table 3* (Mixture #'s are experimental numbers)

<div align="center">

Table 3

</div>

Mixture	polymer 1193	polymer A	alkylphenol	UV9385C	Viscosity
-2950	88	10	2	1	95 cstk
-2940	85	10	5	1	101
-2951	88	10	2	2	94
-2952	85	10	5	2	103
-2953	93	5	2	1	83
-2954	90	5	5	1	90
-2955	93	5	2	2	83
-2956	90	5	5	2	89

All the experimental mixtures were clear, free-flowing fluids when prepared. Viscosities of all blends were monitored over several weeks' time while the candidate formulations were kept in light-proof containers at 40°C (Brookfield viscosity was measured at 25°C after which each sample was returned to the controlled temperature bath). A control bath consisting of a

commercial UV epoxysilicone polymer with UV9385C catalyst was included in this study. Our results are depicted in *Figure 7*
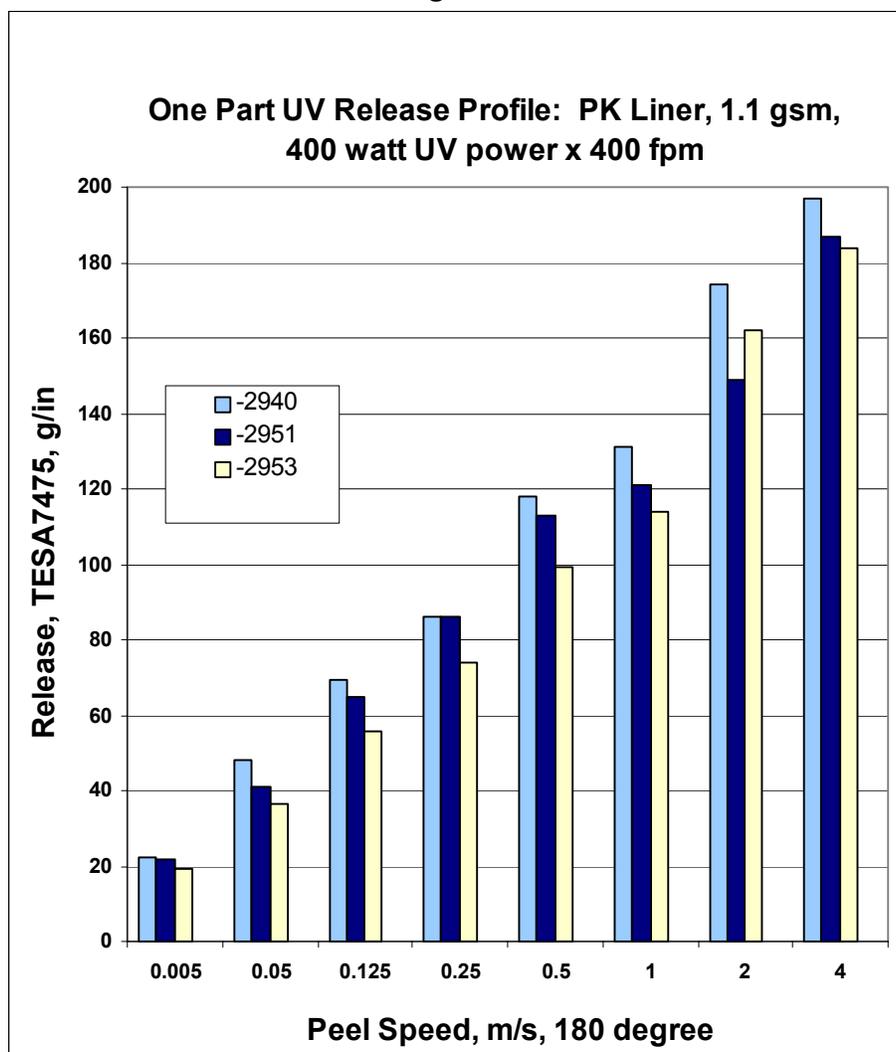
Figure 7

40C Viscosity Build: One Part UV Release Formulae
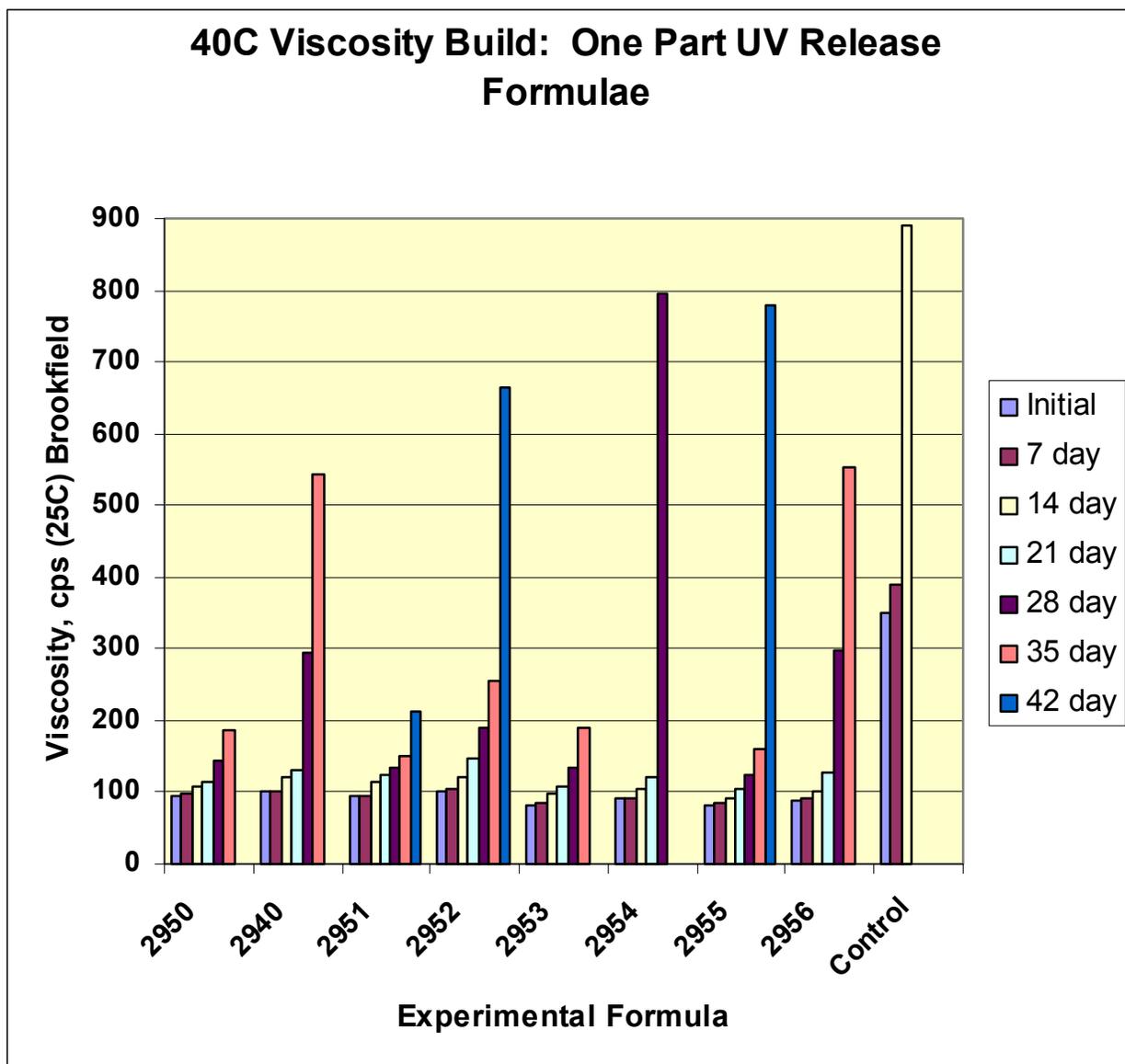
All of the candidate one-part UV release formulas based on Polymer 1193 retained viscosity < 300 cps for at least 4 weeks at 40C, while the control composition was near a gel after 2 weeks' storage under these conditions. Photocatalyst concentration was not a critical variable; shelflife was extended where alkylphenol content was low, and the most stable mixtures had the higher 1193/Polymer A ratio. The difference between the experimental mixtures and the catalyzed control blend is that all of the reactive sites of Polymer 1193 and

Polymer A are at the chain-stopper position…while chain extension takes place during accelerated aging of these 8 coatings, crosslinking to a gel does not occur. Coating and cure trials of three candidate one part formulations were then carried out on the Black Clawson pilot coater with silicone applied to PK at 400 fpm, cured on exposure to 400 watt/in H lamp effective power. TESA 7475 acrylic test tape was applied to the cured silicone offline, the laminates aged 2 weeks, then release of the liners from the tape determined at several peel speeds. The resulting peel release profile is depicted in *Figure 8:*

Figure 8

These peel profiles can be compared to those displayed in *Figure 5*. The one part UV coatings all have a more dynamic profile than that of Polymer 1193 alone. The presence of even as little as 5 parts of long chain dicarbinol-stopped linear PDMS in the coating alters high-speed peel release, presumably because long-chain (>100 D units) linear PDMS segments are included in the cured coating structure. The release performance of the one-part coatings resembles that of conventional thermal cured solvent-free silicone coatings; it is

now possible for converters to easily coat low viscosity silicones on film liners that rapidly photocure to release coatings that mimic thermal silicone performance. Long-term ambient temperature storage of these compositions suggests that a fully formulated shelflife of 9 months to 1 year can be anticipated, as shown in table 4 below:

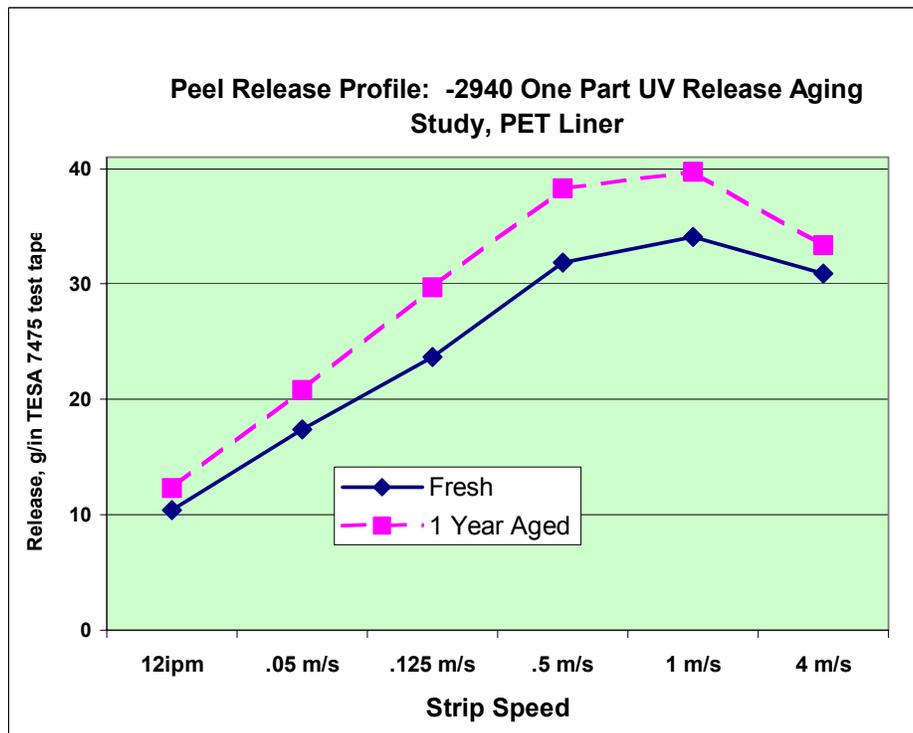**Table 4: One part UV Release Viscosity at 25°C, cps**

Formulation	Initial	3 month	6 month	9 month	1 year
-2940	101	113	153	217	325
-2951	94	98	115	145	202
-2953	83	86	98	138	184

Photo DSC evaluation of freshly prepared one part UV release formulation –2940 was compared with the same measurement of the one year old material. A Perkin-Elmer DSC 7 instrument with photocure accessory (light source was a 100 watt medium pressure mercury vapor lamp) was used for the determinations. Integrated peak area and peak time were compiled, with these results:

Sample	Delta H, J/g	t_{peak}, seconds
Fresh	25.21	7.08
One Yr. @ 25C	11.64	8.64

Based on this result (confirmed by duplicate determinations), it appears that slow chain extension for a year consumes over half of reactive sites present on the two polymers present in the –2940 formulation. Freshly formulated –2940 and year old –2940 were then applied to 2 mil PET liner by means of 3 roll offset gravure technique on the 12 inch pilot coater at GE Silicones in Waterford at a speed of 300 fpm, curing on exposure to one 300 watt Fusion Systems[TM] H lamp. ~ 1.1 gsm was applied to the film in each case without difficulty. TESA 7475 acrylic test tape was used to determine peel release profile after the laminates were aged for a week, as described above. Results of the comparison are displayed in *Figure 9*. Peel profiles are very similar, but some increase in release is evident as the –2940 sample aged over a year. The PET liner is stiffer than PK used in other trials: how the substrate affects peel profile can be seen in comparison of *Figure 8* with *Figure 9.*

Figure 9

Peel Release Profile: -2940 One Part UV Release Aging Study, PET Liner

Release, g/in TESA 7475 test tape

40 —
30 —
20 —
10 —
0 —

Fresh
1 Year Aged

| 12ipm | .05 m/s | .125 m/s | .5 m/s | 1 m/s | 4 m/s |

Strip Speed

Short Chain Silicone Additives in non-Silicone Coatings

There are numerous silicone products available for use as additives in conventional free-radical acrylate coatings. Acrylate- and methacrylate- functional silicone polymers are used to provide slip properties, reduce friction, aid abrasion resistance, improve coating quality, and otherwise modify surface characteristics of compatible photocurable acrylate-based coating formulations. Widely used non-polar acrylate monomers such as HDDA and lauryl acrylate are quite miscible with acrylated silicone fluids and resins. The same is not true of cationic type monomers and oligomers, as the most common of these materials are not miscible with linear PDMS polymers. For example, we found that *all* of the $M^E D_z M^E$ series of polymers prepared in the course of this study, with the exception of the z=0 diepoxydisiloxane, were incompatible with the commercial di-cycloaliphatic epoxy dicarboxylate monomer available from several vendors including Dow Chemical, Sartomer, and others. But non-polar linear silicones have been shown to be miscible with many vinyl ether monomers, and, more recently, with oxetanes (2, 3). Much has been published about the use of compatible vinyl ether monomers (mono and polyfunctional) as *additives* in conventional epoxysilicone release coatings. We therefore decided to study the effects of short-chain epoxysilicone polymers as additives in vinyl ether based coatings. Two difunctional vinyl ether monomers that are miscible with polymer 1193 were selected for study: 1,4-cyclohexanedimethanol divinyl ether (CHVE) and 1,6-hexanediol divinyl ether (HDDVE).

CHVE and HDDVE are reactive compounds. Addition of 1% of the photocatalyst package UV9390C to either monomer resulted in a curable mix that cured to a hard, glossy thin coating on PET upon exposure to < 25 mJ/cm^2 focused UV light in the lab RPC Processor. Blends or either divinyl ether with Polymer 1193 epoxy-stopped silicone were prepared with silicone content ranging from 5 to 50%; all mixtures cured as rapidly as the vinyl ether monomer alone under the same catalysis and UV exposure conditions. It should be noted that these mixtures are all very low viscosity fluids (< 20 cstk @ 25C) easily applied to plastic and film substrates by direct gravure, flexo, and spray techniques. We sought to determine the minimum level of epoxy-stopped silicone in CHVE or HDDVE coating necessary to impart silicone properties to a photocured coating surface. Simple coatings of various blends of Polymer 1193 with CHVE ~ 2 g/m^2 coatweight were prepared on PK substrate, cured by minimal UV light exposure, then analyzed for surface composition by AT-FTIR technique. Spectra so obtained are displayed in *Figures 10 – 12.*

Figure 10: Full AT-FTIR Spectra of CHVE-1193 Blend Coatings
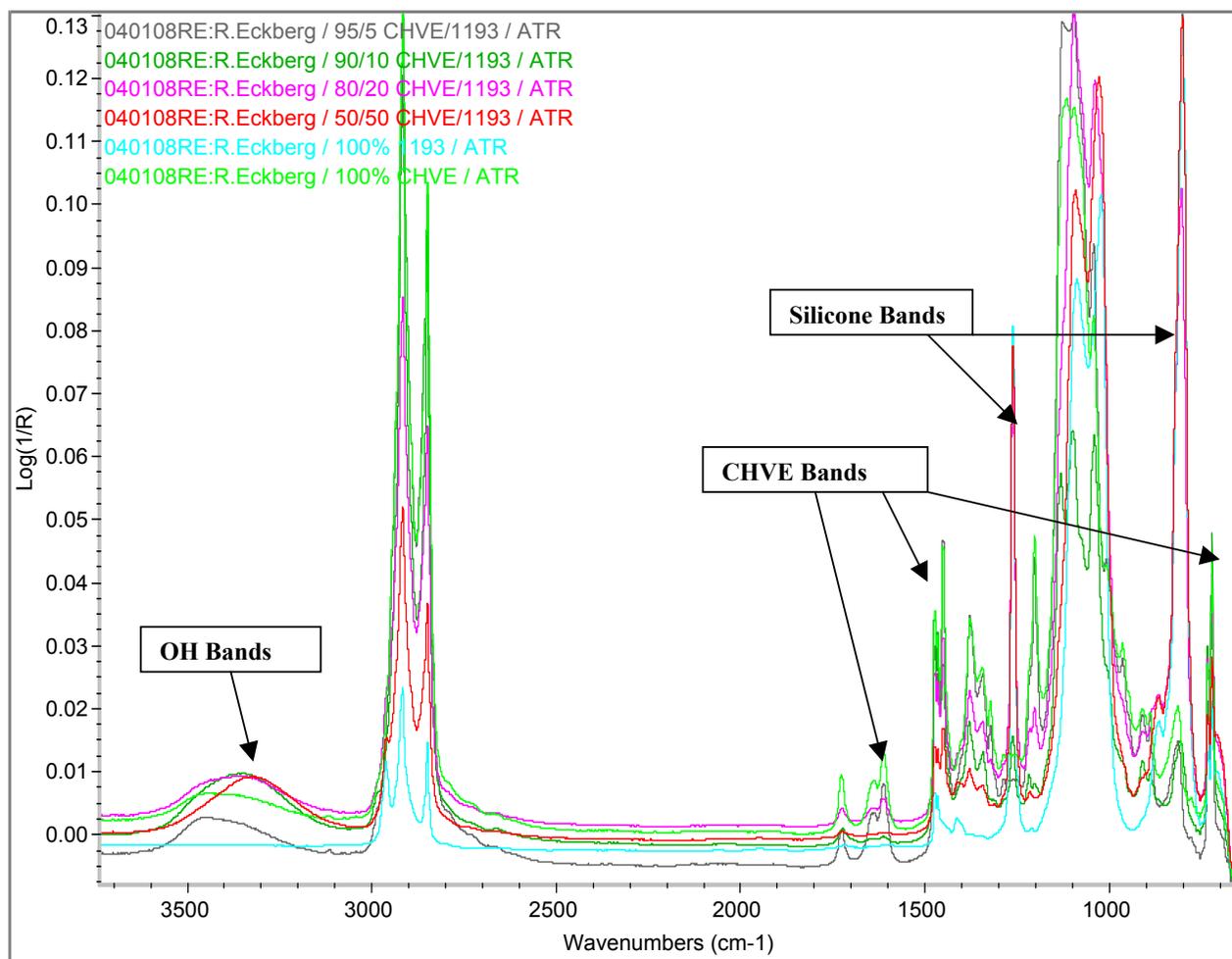
Examination of Specific wavelength regions of these spectra clarifies the effect of composition on the surface of the cured coatings.

**Figure 11: 1150 – 1300 cm^{-1} Region**
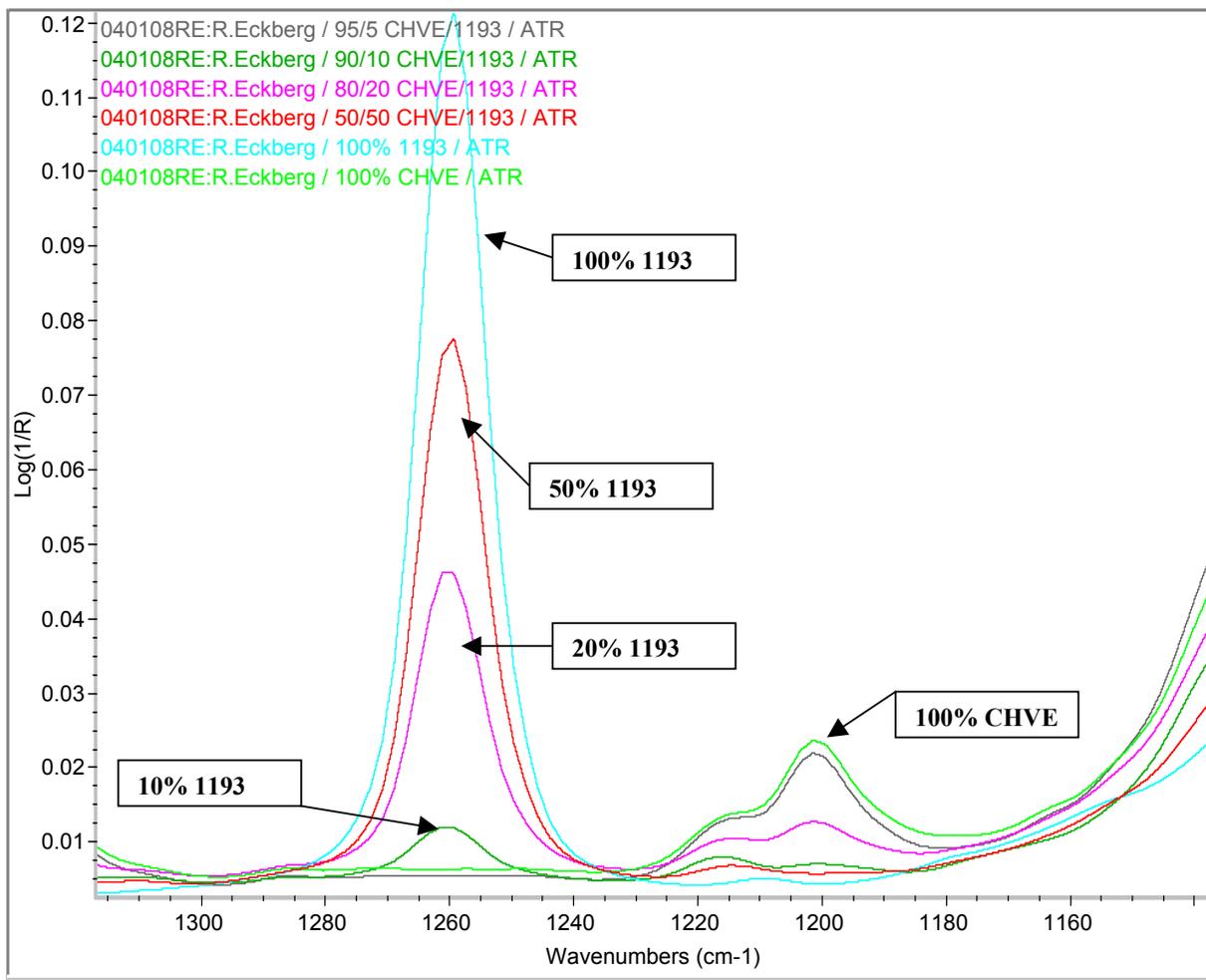
It is apparent from the expanded spectra that there is significant silicone present in the coatings' surface if 10% or more Polymer 1193 is in the CHVE/1193 coating mixture. We observed an unexpected trend in the spectral region > 3000 cm^{-1} as shown in *Figure 12*. The broad bands at 3300 – 3400 cm^{-1} are –OH stretch often associated with water. Vinyl ethers' cationic cure is retarded by the presence of moisture, but if there were a 'water effect' on the surface composition of these photocured mixtures, we would expect it to be apparent as a function of VE content. Instead, the biggest OH band is found in the 50/50 blend coating. We cannot account for this observation; there is no OH band in the 100% silicone coating surface IR spectrum, and only a weak band in the 100% CHVE surface. A summary of AT-FTIR absorbances of interest is presented in **Table 5** below:

Table 5

| SAMPLE	OH Stretch Band Region (3700 cm^{-1} – 3050 cm^{-1})	Si-CH3 Stretch Band Region (1280 cm^{-1} – 1234 cm^{-1})
100% CHVE	0.563	0.025
100% UV1193	0.053	1.708
95/5 CHVE/UV1193	0.692	0.030
90/10 CHVE/UV1193	1.641	0.121
80/20 CHVE/UV1193	1.100	0.604
50/50 CHVE/UV1193	2.169	1.077

Figure 12
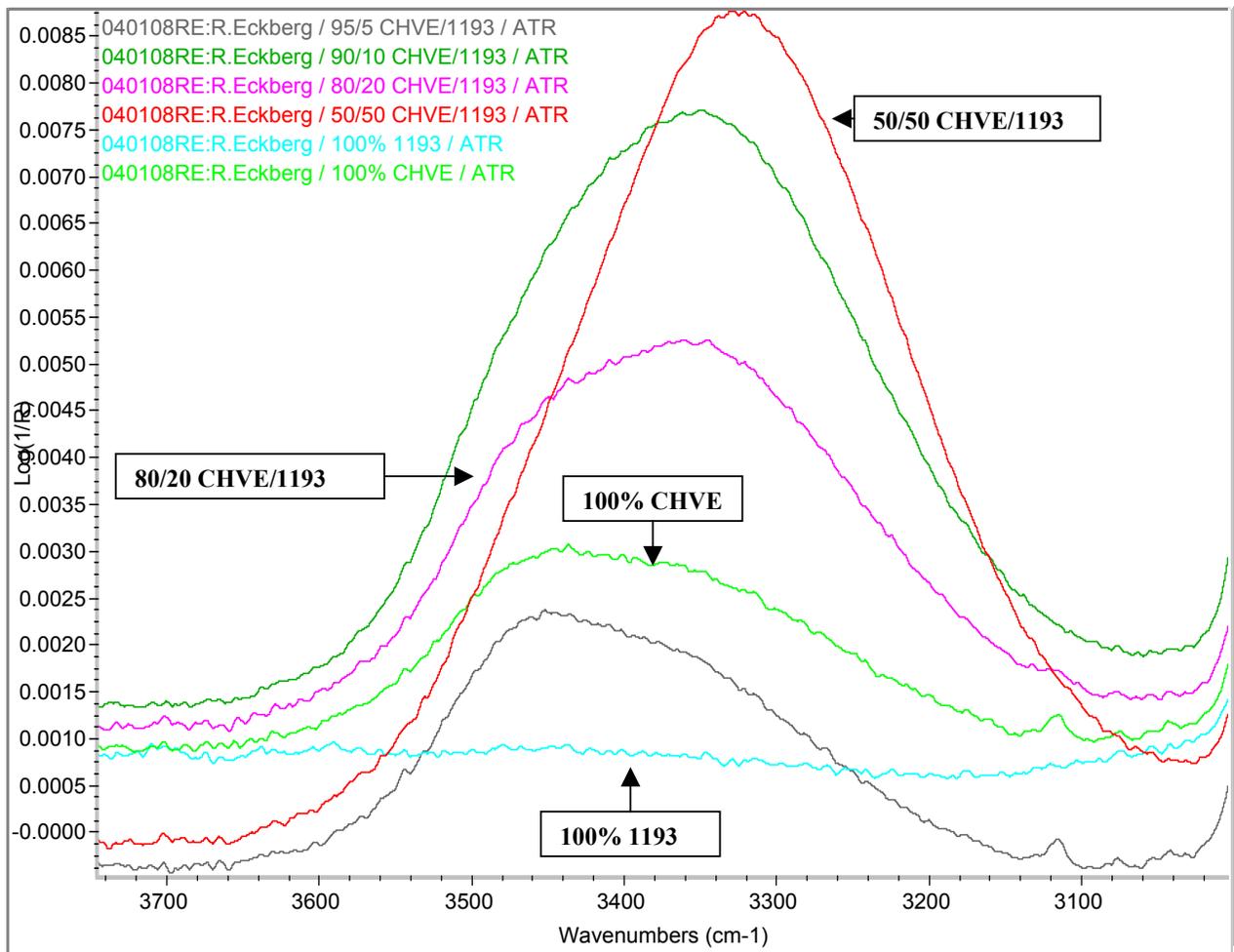
The same CHVE/Polymer 1193 blend coatings described above were also applied to a 2.5 mil PET at ~ 1.2 g/m^2 coatweight, photocured and laminated with TESA7475 acrylic test tape to determine if coatings with low levels of silicone could function as release coatings. Peel speed profiles were recorded for those coatings that released the tape

(coatings with < 10% Polymer 1193 present did not release TESA 7475 test tape after a week of laminate aging under weight, consistent with the FTIR spectral indication of very little silicone presence in coating surface for those mixtures). Profiles are shown in *Figure 13.*

Figure 13

Peel Release Profiles of CHVE + Polymer 1193 Coating Blends: 1.2 gsm on 2.5 mil PET
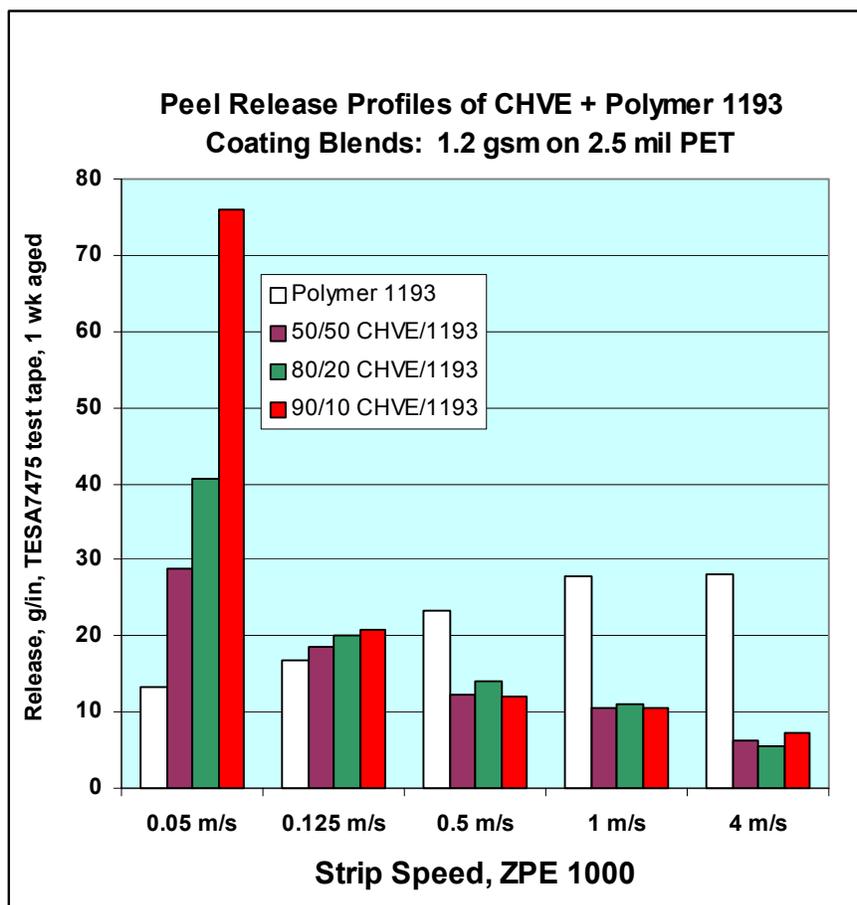
The aggressive test tape required a big initial energy input to initiate peel (called an 'initiation spike') from the 10% silicone coating that was most pronounced at low peel speed. A decline in release as a function of peel speed is frequently observed for high modulus coatings, as previously reported. 'Release' from the 90% and 80% CHVE coatings was observed to be 'zippy', and different in character than conventional release behavior, but once initiated, did not require undue force to maintain.

Besides release, the presence of Polymer 1193 in cured CHVE coatings provides modification of slip properties as measured by Coefficient of Friction. CoF measurements utilized a weighted sample of uncoated PK substrate being dragged across the cured coatings (coated on the same PK substrate). Average and Peak CoF were recorded in triplicate; results are graphically depicted in *Figure 14.*
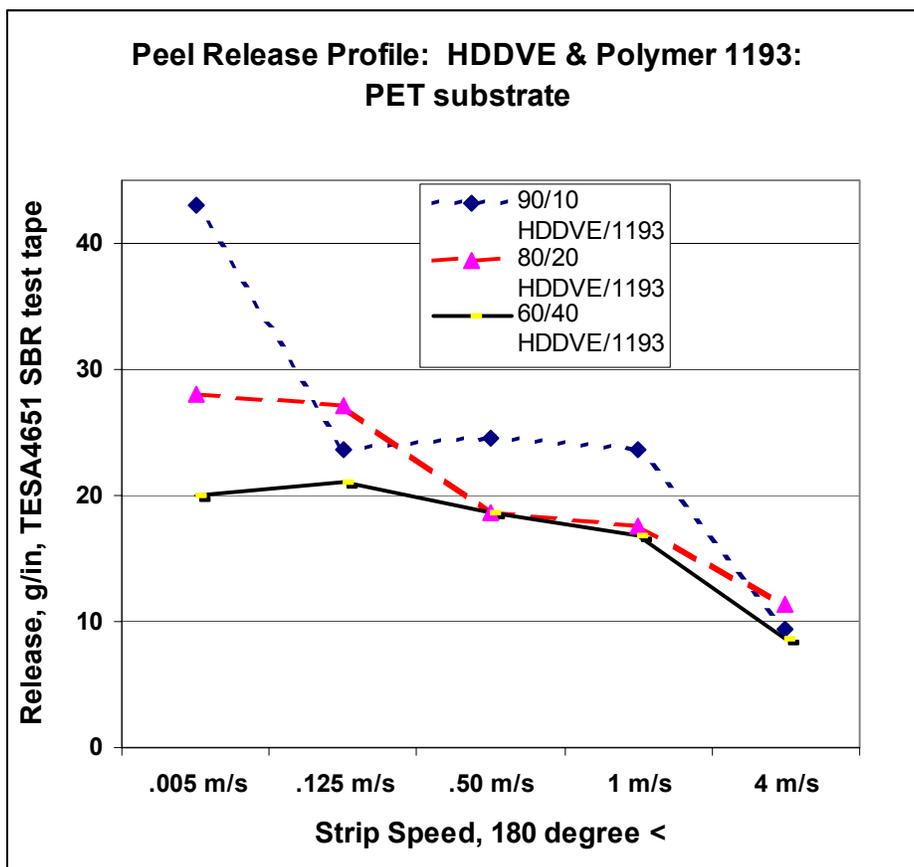
Figure 14

Slip Properties of CHVE + Polymer 1193 Coatings, PK Substrate
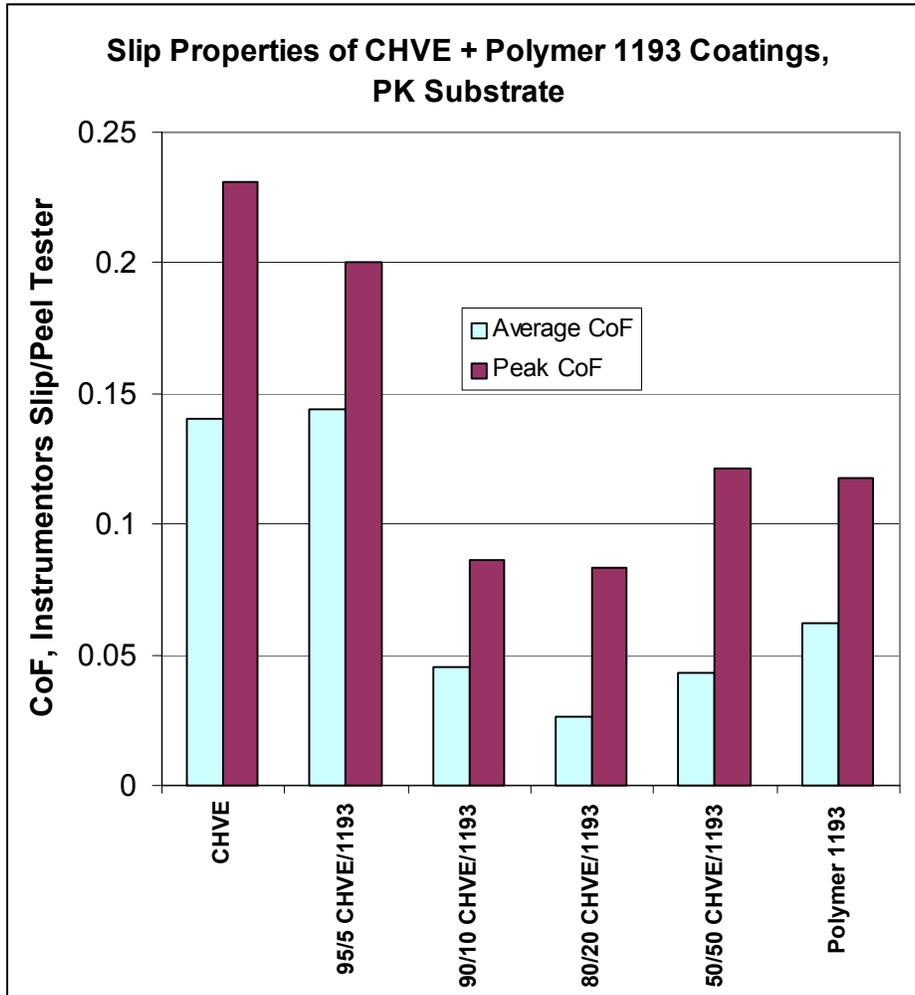
As was the case for release from the acrylic test tape, the blend coatings required at least 10% silicone content to modify slip properties.

Coatings of a series of catalyzed blends of HDDVE with Polymer 1193 were applied to a 1.5 mil PET substrate and cured in the same fashion as the CHVE/1193 coatings. TESA 4651 SBR type adhesive test tapes were applied to the cured coatings and the laminated tapes aged under ambient conditions under weight for a week, then peel profiles were recorded as above. The rubber based PSA released from all coatings tested, including the coating of neat HDDVE, though separation of the tape from the silicone-free surface was too difficult for accurate measurement. Graphical depiction of Peel Release Profile of TESA4651 from selected cured coating blends of HDDVE + Polymer 1193 is displayed in *Figure 15.*

Figure 15

Peel Release Profile: HDDVE & Polymer 1193: PET substrate

(Y-axis: Release, g/in, TESA4651 SBR test tape; X-axis: Strip Speed, 180 degree <; Legend: 90/10 HDDVE/1193, 80/20 HDDVE/1193, 60/40 HDDVE/1193; X-axis values: .005 m/s, .125 m/s, .50 m/s, 1 m/s, 4 m/s)

Cured, coated blends including 10 to 20% Polymer 1193 mixed with either of the divinyl ether monomers accept ink, so these coatings can function as photocurable *printable* release surfaces.

Silicone Polyether Additives in Cycloaliphatic Epoxy Resins

As noted above, cycloaliphatic epoxy-stopped linear PDMS polymers $M^E D_z M^E$ where z>0 are immiscible with the most widely used dicycloaliphatic epoxy compound 7-oxabicyclco[4.1.0]heptane-3-carboxylic acid, 7-oxabicyclo[4.1.0]hept-3-ylmethyl ester (Dow Chemical Cyracure^{TM} Cycloaliphatic Epoxide Resin UVR-6105, also available from other vendors under different product names) and are not useful additives in coatings based on such materials. Incorporation of curable linear silicone properties into conventional UV cure cycloaliphtic epoxy resin coatings requires polar organofunctionality plus reactive –OH or epoxy sites be present on the silicone molecule. Linear epoxy-stopped block copolymers of poly(dimethylsiloxane)-poly(ethyleneoxide) have been described and shown to be useful-stand alone coatings with excellent miscibility in many non-silicone epoxy resins (15, 16), but such compounds are not extant commercially. Well-known silicone products miscible with the epoxy resins and photocurable with the epoxies are silicone-polyether surfactants

developed for use in cosmetic applications and for processing of polyurethane foam. Silicone-polyethers are prepared by hydrosilation reaction of SiH- functional silicone polymers or oligomers with unsaturated polyethers, usually alkoxylated allylalcohols, as shown below:

$$\equiv SiH + CH_2=CHCH_2(OCH_2CHR)_aOH \rightarrow \equiv Si(CH_2)_3(OCH_2CHR)_aOH$$

where R = H or alkyl. Depending on the structure of the SiH silicone precursor polymer, the resultant silicone polyethers can be 'comb' type structures such as $MD_iD^{PE}{}_jM$ ('PE' refers to polyether function), or linear block copolymers: HO-PE – D_k – PE-OH, or a combination of these structures. A commercial 'comb' type silicone polyether was selected for a series of blend experiments with UVR6105 cycloaliphatic epoxy resin. The silicone polyether was of structure $MD_{15}D^{PE}{}_5M$, and 'PE' was approximately $–(CH_2)_3(CH_2CH_2O)_{13}OH$. The polymer therefore was about 1/3 PDMS and 2/3 polyether, with Hydroxy Equiv. Weight ~ 900. We found that this product was nicely miscible with UVR6105. Accordingly, different blends of the two materials were prepared with 1 part of neat (4-octyloxyphenyl) phenyl iodonium SbF_6 (OPPI) photocatalyst present per 100 parts of blend. 2 mil thick coatings of the catalyzed mixtures were applied to PET substrate using a Gardner Applicator, the coated PET then exposed to a 200 watt/in focused UV light in the RPC Processor as described above. The number of passes through the device at 100 fpm conveyer speed (~ 120 mJ/cm^2 per pass) required for tack-free through-cure (per thumb twist evaluation) were recorded, with results displayed in Table 6:

Table 6: Cure of UVR6105/'Comb' Silicone PE blends on PET

Parts UVR6105	Parts Silicone PE	Conveyer Passes
100	0	3
90	10	4
80	20	7
50	50	9

Photocure response slowed considerably as OH/Epoxy increased, even though the OH/epoxy ratio was 1/7 or lower for all blends. Neither TESA 7475 acrylic or TESA 4651 SBR test tape would release from any of these cured coatings, so such blends are not likely candidates for printable liner manufacture. Differential PhotoCalorimetric Data (@ 30°C) did not reflect the qualitative cure observations tabulated above, as depicted in *Figures 16 & 17.* Peak exotherm did not slow for the 50/50 mix versus 100 % UVR6105, and, as expected, total Delta H increased somewhat as reactive –OH sites were included in the curable matrix. 'Postcure' response was also about the same. An interesting observation was that the presence of the silicone surfactant diluent markedly improved wet-out of the UVR6105 on the polyester substrate, and the cured coatings with silicone-polyether present had a smoother appearance and better optical clarity. So, silicone polyethers can be considered curable coating additives for cationic UV cure coatings that improve flow-out and coating quality.
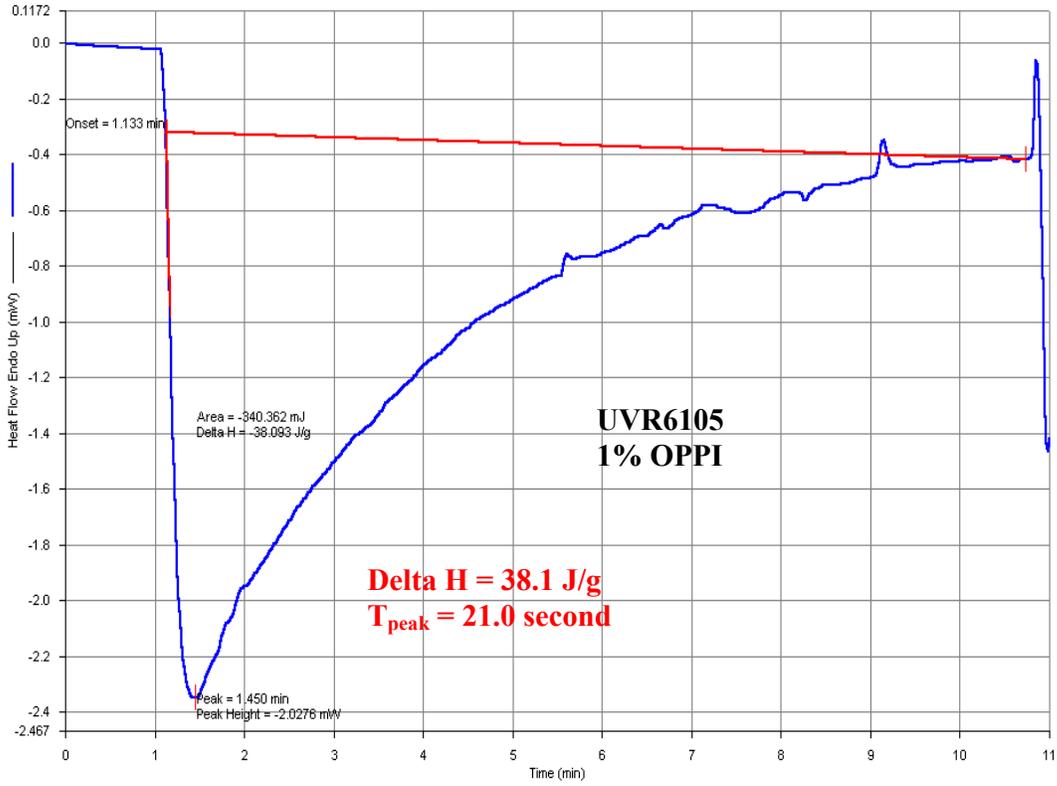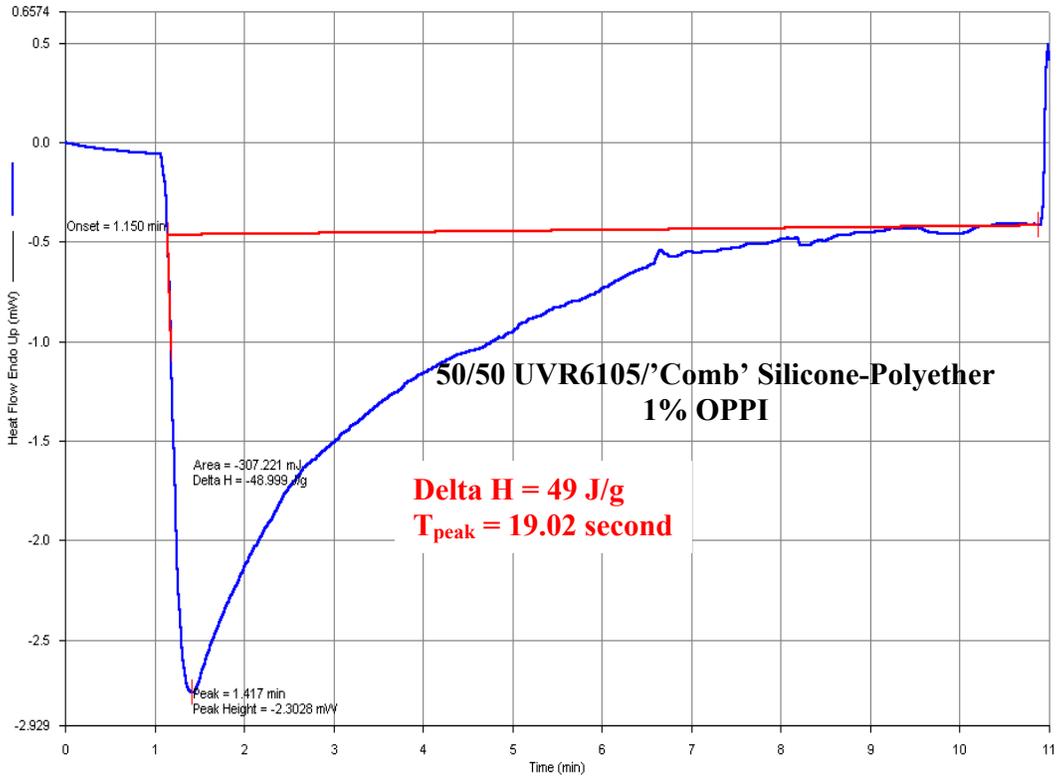
Figure 16

Onset = 1.133 min

Area = -340.362 mJ
Delta H = -38.093 J/g

**UVR6105
1% OPPI**

**Delta H = 38.1 J/g
T$_{peak}$ = 21.0 second**

Peak = 1.450 min
Peak Height = -2.0276 mW

Figure 17

Onset = 1.150 min

Area = -307.221 mJ
Delta H = -48.999 J/g

**50/50 UVR6105/'Comb' Silicone-Polyether
1% OPPI**

**Delta H = 49 J/g
T$_{peak}$ = 19.02 second**

Peak = 1.417 min
Peak Height = -2.3028 mW

Coatings of these blended materials were examined for silicone surface effects, but no clear trend was observed from CoF measurements. Given the structure of the 'comb' type silicone-polyether, there is on average only 2 – 3 'D' units in PDMS segments between sites occupied by the PE chains, probably not long enough to provide 'silicone-like' properties at coating surfaces. We therefore extended our study to include a different type of silicone-polyether, a linear block cpopolymer structure depicted below:

$$HO-(CH_2CH_2O)_{7.5}-(CH_2)_3-(CH_3)_2SiO\{D\}_{10}Si(CH_3)_2-(CH_2)_3-(OCH_2CH_2)_{7.5}OH$$

This commercial product has Hydroxy Equivalent Weight of ~ 825, and is about ½ silicone and ½ polyether. Miscibility with UVR6105 was limited to 50 wt % (higher percentages of the linear silicone-polyether phase-separated from the diepoxide), another demonstration of just how incompatible PDMS and highly polar organic molecules are. 100/0, 80/20, and 50/50 blends of UVR6105 and the linear PDMS-PE were prepared with 2 phr of UV9390C catalyst added to each. Photoresponse of each catalyzed mix was determined using DPC and Gelpointe^{TM} instrumentation. The Gelpointe apparatus provides for isothermal measurement of gel time under white light irradiation. UV9390C includes a thioxanthone sensitizer that responds to visible light, making GelPointe oberservations useful for comparative purposes. Results of these analyses are noted in Table 7.

Table 7: PhotoResponse of UVR6105 blends with Linear PDMS-PE

| Mixture	DPC DeltaH	DPC t_{peak}	GelPointe Gel Time
100% UVR6105	132.4 J/g	12.54 sec.	383 sec.
80% UVR6105	132.0	11.90 sec	174
50% UVR6105	133.2	11.52 sec	177

The presence of sensitizer speeds the photoresponse versus that of the UVR6105 – silicone polyether blends catalyzed with OPPI alone (displayed in *figures 16 & 17* above). The linear silicone PE can be used with compatible cycloaliphatic epoxy compounds in photocurable coatings without loss of cure; the Gelpointe data suggest presence of the linear silicone PE additive speeds crosslinking. 2 mil coatings of three formulations incorporating 0, 10, and 20% linear silicone PE were then applied to PET with the Gardner Applicator and through-cured by 4 passes through the RPC Processor as described above. A significant improvement in wet-out and coating appearance were realized by addition of the linear silicone-PE. The cured coatings were then analyzed for friction behavior. Uncoated PET was weighted and drawn across each coated sample at a constant rate with CoF recorded on the Instrumentors device. Results are included in Table 8.

Table 8: CoF of UVR6105 blends with Linear PDMS-PE (Avg of 4 determinations)

| Mixture	Average CoF	Peak CoF
0% PDMS-PE	.066	0.117
10% PDMS-PE	0.019	0.051
20% PDMS-PE	0.022	0.059

The CoF results are not conclusive, but indicate that the linear PDMS-PE additive does inculate silicone properties in the UVR-6105 coating surface. AT-FTIR spectral analyses confirm that significant PDMS is extant in those coatings including the linear PDMS-PE block copolymer, as displayed in *Figure 18.*

Figure 18: AT-FTIR of Coating Samples, 1800 – 650 cm^{-1}
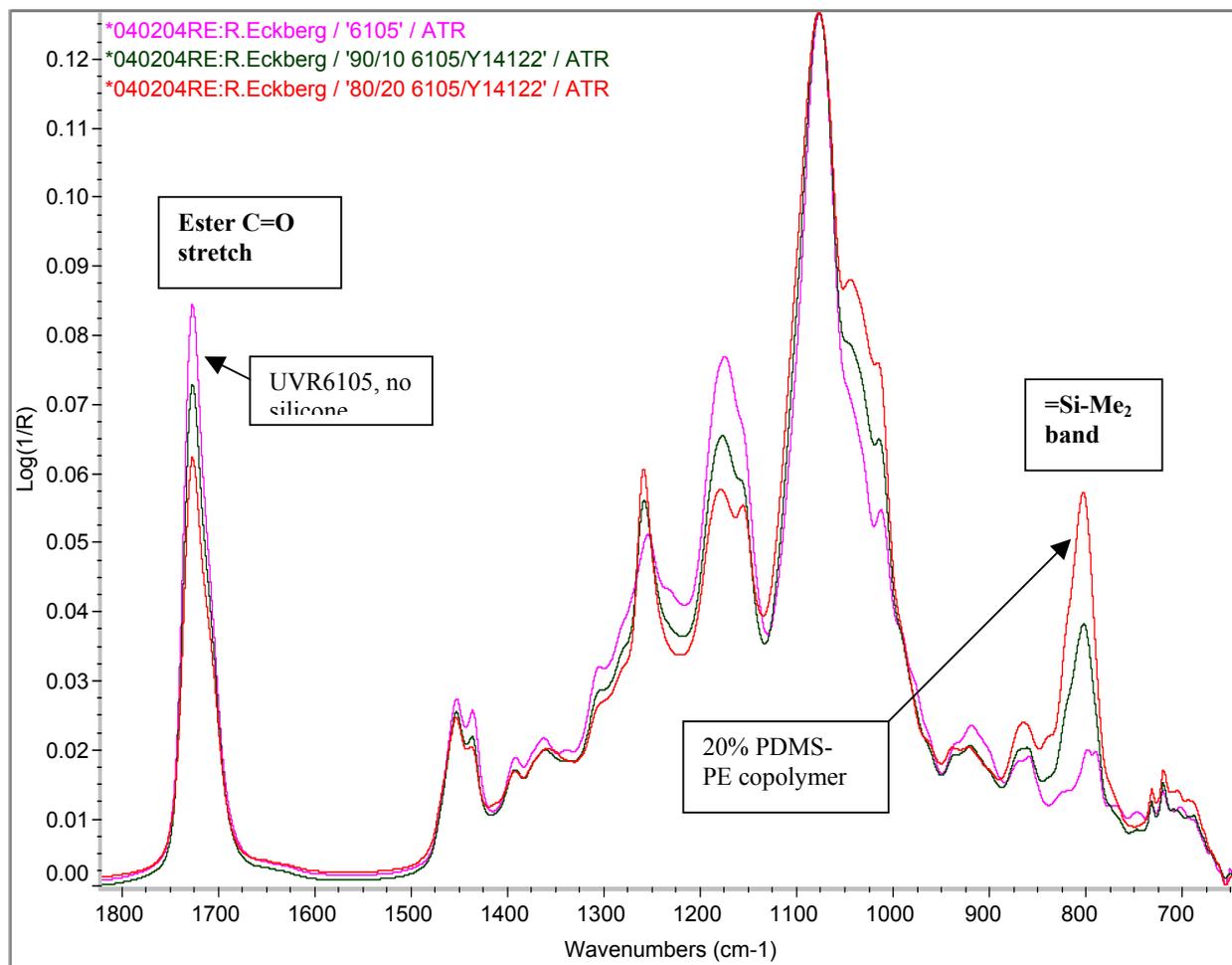
The spectral analysis results are similar to those obtained for the CHVE-Polymer 1193 coatings described above, as is the peel release profile of TESA 7475 acrylic test tape from the 80/20 UV cured coating of UVR6105/linear PDMS-PE, displayed in *Figure 19.* Release of this tape from the coating was very 'zippy' and difficult to initiate at low peel speed. TESA 4651 SBR type test tape did not release well at all. So, while low levels of the block copolymer (HO) PE – PDMS – PE (OH) polymer effectively provide silicone slip and wet-out properties to di-cycloaliphatic epoxy monomer based UV cured coatings, the blends tested in this study are far from being useful for conventional release of PSA's. More work is needed to design a silicone polymer compatible with and curable with conventional cationic epoxy coating materials if such blends are to be acceptable replacements for 100% silicone coatings.

Figure 19

Release Profile: 80/20 UVR6105/Linear PDMS-PE Coating on PET
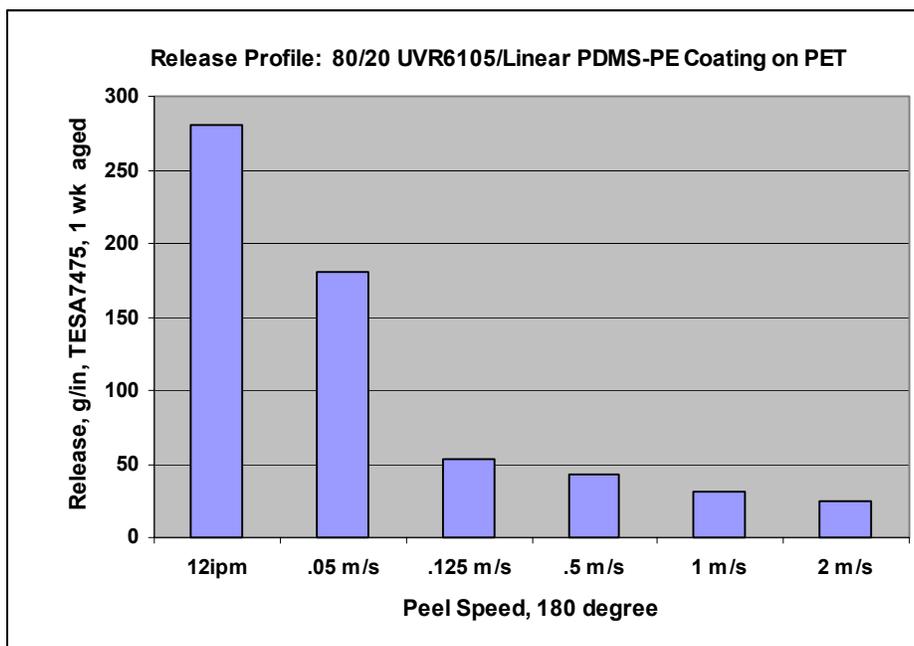
Summary and Prospectus

Representative short-chain silicone polymers have been studied for photocurable coating applications. Linear cycloaliphatic epoxy-chainstopped PDMS has been shown to be a useful additive for commercial cationic type UV curable epoxysilicone release agents, an essential input for design of shelf stable one-part UV cure cationic type coatings, and capable of modifying slip and release properties of compatible vinyl ether monomer-based coatings. We have also shown that hydroxy-functional short chain silicone-polyether copolymers can be added to conventional non-silicone cationic cycloaliphatic epoxy coatings to impart silicone character to cured coatings derived therefrom without compromise of photocure performance. Further work in this area will be for design of reactive organofunctional silicones with longer linear PDMS segments still possessing good miscibility with common non-silicone cationic type radiation curable coatings.

Acknowledgements

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