

## **Release coatings: Defining Performance**

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### **Abstract**

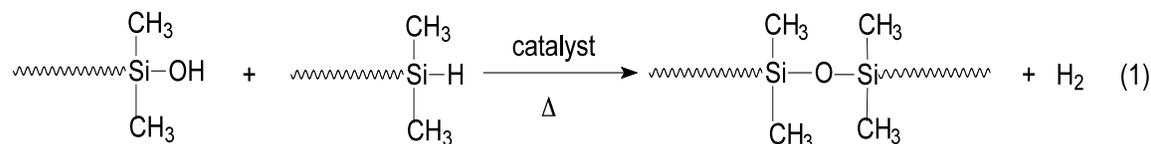
Films with release coatings are in strong demand for a wide range of applications from window films to flexible displays. In searching for replacements for tin-based catalysts used to cure liquid silicone coatings applied to film substrates such as PET, we aim to preserve the essential characteristics of the “Sn”-cured coatings. These include extractables, the expected peel release values (PRV) of calibrated test tapes, expected PRVs of laminates with selected adhesive(s), and the retention of such properties for twelve months or more. Measurements of peel release values highlight the difficulty of defining the performance of a release surface.

### **Introduction**

Release films are prepared mainly in two ways: photopolymerization (UV-cure) of silicone acrylates or of silicone oxiranes (epoxies) and by thermal cure of siloxanes (silicones). The first method utilizes either free-radical or cationic polymerization. Thermal cure is accomplished either by dehydrogenative condensation of hydroxyl-terminated silicones or by hydrosilylation of vinyl-terminated silicones.<sup>1,2</sup> Despite many advantages of photopolymerization, such as fast process and no VOC releases, coatings prepared by thermal cure are in strong demand in the market because of their particular combination of performance properties. In this work we studied mainly raw materials and base formulations of thermal cure release coatings available by Momentive (Waterford, New York).<sup>3</sup>

Liquid formulations of release coatings usually have a high concentration of hydrocarbon solvents. Solvents evaporate, and they are incinerated during cure. Solvent-

borne formulations allow very thin release coatings to be deposited with a thickness less than 100 nm. Tin-catalyzed thermal cure of siloxanes is a reaction between a silicone diol ( $\alpha,\omega$ -dihydroxy-terminated PDMS, *silanol*) and a relatively low molecular weight silicone with hydro- and methyl groups (*silane*). Cure is a dehydrogenative condensation:



We will focus in this presentation on cure according to reaction (1). Reaction (1) is crosslinking because the functionality  $f$  of reagents is more than one: silanol has  $f_{\text{OH}} = 2$  and that of silane  $f_{\text{H}} > 2$ . The silane is taken in excess in order for crosslinking to compete with self-condensation of silanols. The reaction is catalyzed by tin compounds such as dibutyltin diacetate (“Sn”) and proceeds during 10-100 s at elevated temperatures ( $\sim 150$  °C) once solvents have been removed.

## Results and Discussion

We studied in this work three different formulations prepared according to recommendations in ref. 3. The most significant difference between these three formulations is a concentration of control release additive (CRA) that increases the peel release force of adhesive bonds to the release coating. Concentration of CRA in each of three coatings is presented in the Table 1 below:

Table 1

**Percents of solids in Coatings 1-3**

Coating	Total percent of solids	CRA, percent of solids on solids
<b>1</b>	<b>7.1</b>	<b>0</b>
<b>2</b>	<b>8.3</b>	<b>15</b>
<b>3</b>	<b>8.5</b>	<b>26</b>

IR-ATR spectra of reaction mixtures can be used to demonstrate the extent of reaction of the silane component by monitoring the  $\nu(\text{Si-H})$  signal at  $2240\text{ cm}^{-1}$  (Figure 1)

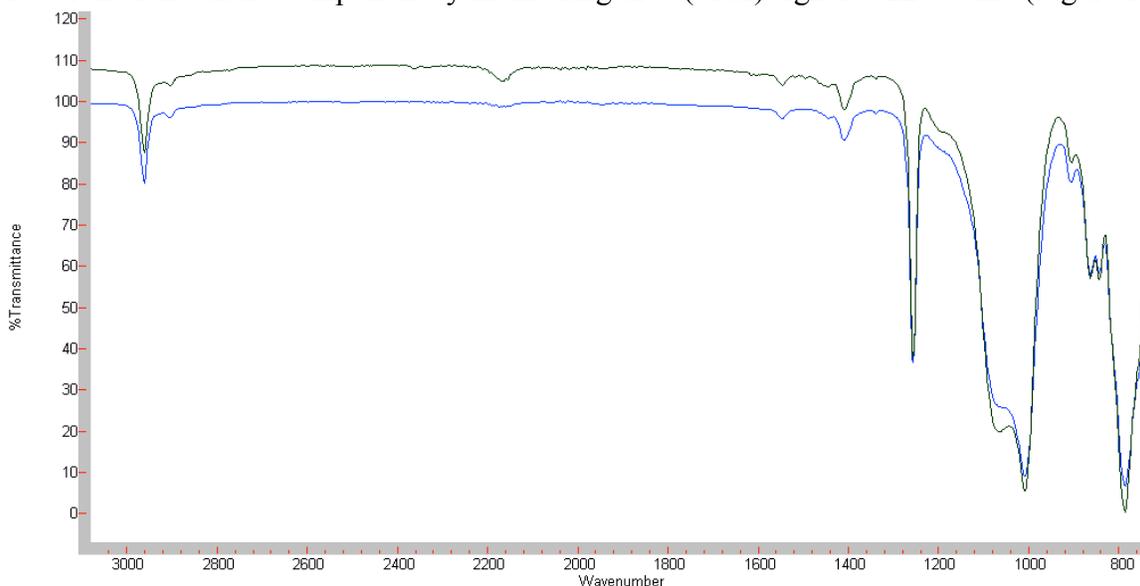
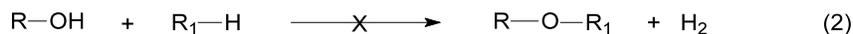


Figure 1. IR-ATR spectra of the coater-ready liquid formulation for Coating 3 taken promptly after hydrocarbon solvents evaporated from the diamond ATR crystal. Top curve is a spectrum of the freshly evaporated solution; the bottom curve is a spectrum after solvent evaporation of the same coater-ready sample kept for 4 days after preparation at ambient conditions. Wavenumber is in  $\text{cm}^{-1}$

Release coatings based on a reaction (1) are widely used in the industry.<sup>1-8</sup> Despite that fact, the mechanism of reaction (1) is not clear. The analogous reaction between an aliphatic alcohol (ROH) and a hydrocarbon (RH) does not occur:



Consideration of bond dissociation energies (BDEs) demonstrates that reaction (1) is almost thermoneutral whereas reaction (2) is strongly endothermic. The main reason is that the C-O BDE in an ether is 58-86 kcal/mol, whereas the Si-O BDE of “silicon ether” is 106-108 kcal/mol, and the formation of “silicon ether” leads to a higher energy gain compared with the formation of ether.

Formulations that have low amounts of solvent gel during storage under ambient conditions after a few days or a week. High concentrations of reagents in such solutions facilitates the bimolecular reaction (1).

An important numerical characteristic of a release liner is its peel release value (PRV). This is the force required to peel an adhesive from a release liner and is traditionally measured in g-force/in. ( $\text{N/m}$  or  $\text{kg/s}^2$  in SI). Popular test tapes used in the industry are 610 tape of 3M and Tesa<sup>®</sup>'s 7475 or 7476 tapes.

Manufacturers of release liners are familiar with a number of problems relating to PRV measurement and the use of test tapes. Properties of a test tape vary from tape to tape; in addition they change with time. Measurements of PRV with a peel tester such as the Imass SP-2000 or 2100 of IMASS inc. lead to large determination errors unless steps are taken to reduce them. We consider a standard deviation of not more than 20% of the average PRV value determination as acceptable. Immediate testing of release liners after production leads to unreliable data with a very large scatter because properties of the liner have not yet reached a constant level. Release liners, like most quickly cured coatings, undergo post-polymerization for at least several days.<sup>9,10</sup> Less scatter of peel release values is observed with samples aged for several days. In our experiments with Coatings 1-3, the standard deviation of PRV decreased 1.5-2 times after aging liners for 5 days at ambient conditions.

In measurements of PRV with the Imass SP-2000 the peel off angle increases during a measurement:

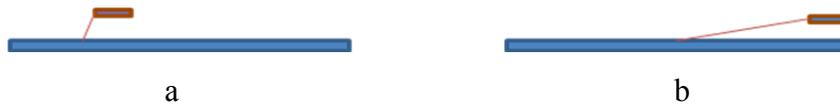


Figure 2. Pictorial representation of PRV measurement with the Imass SP-2000. The peel off angle increases during measurement, compare Figures b and a.

An increase of peel angle often leads to an increase of PRV. Figure 3 presents a characteristic case for Coating 1 as an example:

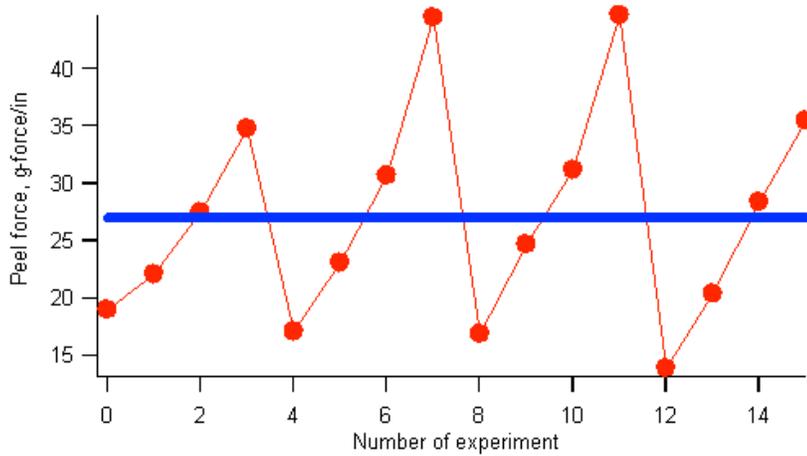


Figure 3. Dependence of PRV on peel angle. Measurements were done for four samples of Coating 1 (cf. below) with Tesa 7475 tape. Four readings were taken on each film

We have found that placing of a light cylinder between the delamination point and the film grip of the Imass SP-2000 reduces the peel angle dependence, cf. Figure 4.

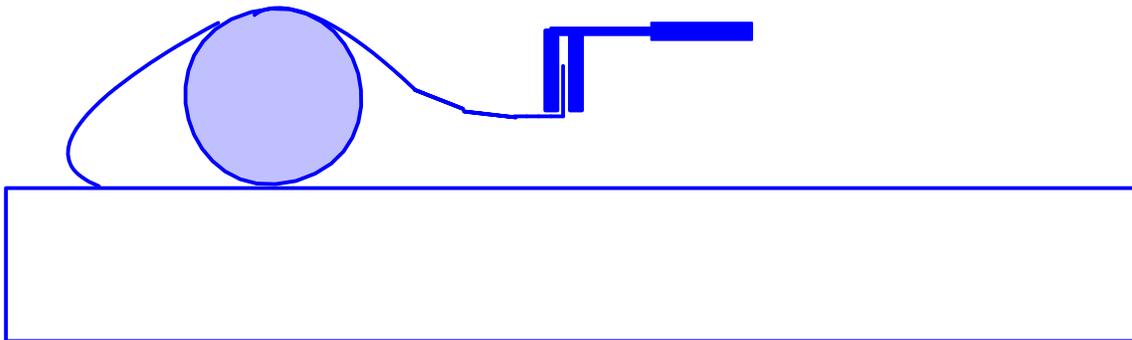


Figure 4. Pictorial representation of a PRV measurement with the Imass SP-2000 which uses a cylinder to reduce the variation of peel angle. The fixed height of the cylinder, which rolls in the direction of peel during the test, maintains the angle of approximately 45° between the film and test platen.

Table X below demonstrates the difference in PRVs in the presence and absence of a cylinder:

Table 2

**PRVs for the Coating 3 versus Tesa tape with and without  
a cylinder of diameter 10 mm**

PRV, g-force/in	Determination error <sup>a</sup> , %	Cylinder
43	51	No
35	17	Yes

<sup>a</sup>The determination error is the standard deviation of the measurement as a percentage of the mean value.

PRV depends upon parameters which makes a task of its reliable determination rather complex. PRV depends upon relative humidity (RH), temperature, age of the liner and age of the adhesive bond between liner and test tape, rate of peel off and any conditioning of a liner with an adhered tape. Regarding conditioning, in particular, FINAT test method #3 teaches to keep a liner with the adhered tape for 20 h at RH= 50% and under a pressure of 70 g-force/cm<sup>2</sup>. Prior to measurements, the liner/tape should then be kept for at least 4 h at room temperature with no load applied. Our experiments demonstrate that such conditioning increases PRV by as much as 27 times, cf. Table 3 below:

Table 3

**PRVs obtained for Coatings 1-3 with Tesa tape not-conditioned and conditioned according to the FINAT test<sup>a</sup>**

Coating	Conditioned	PRV, g-force/in	Determination error, %	Increase of PRV after conditioning, times
1	No	16	20	-
1	Yes	428	18	27
1	Yes <sup>b</sup>	570	23	36
1	No	27	30	-
1	Yes	357	25	13

2	No	27	15	-
2	Yes	387	18	14
2	Yes <sup>b</sup>	580	26	21
2	No	55	27	-
2	Yes	113	57	2
3	No	132	25	-
3	Yes	292	36	2
3	No	78	41	-
3	Yes	160	34	2
3	Yes <sup>b</sup>	710	20	9

<sup>a</sup>Two independent measurements were done on the films with a same coating

<sup>b</sup>Measurements were taken on the film after 6 months storing the film under ambient conditions with the test tape attached

The presence and concentration of a control release additive (CRA) obviously affects the PRV. Momentive<sup>3</sup> recommends silicone MQ-resin **SS4215** as CRA. We have verified the CRA effect on PRV in three formulations with Tesa 7475 and with 3M 610 tape:

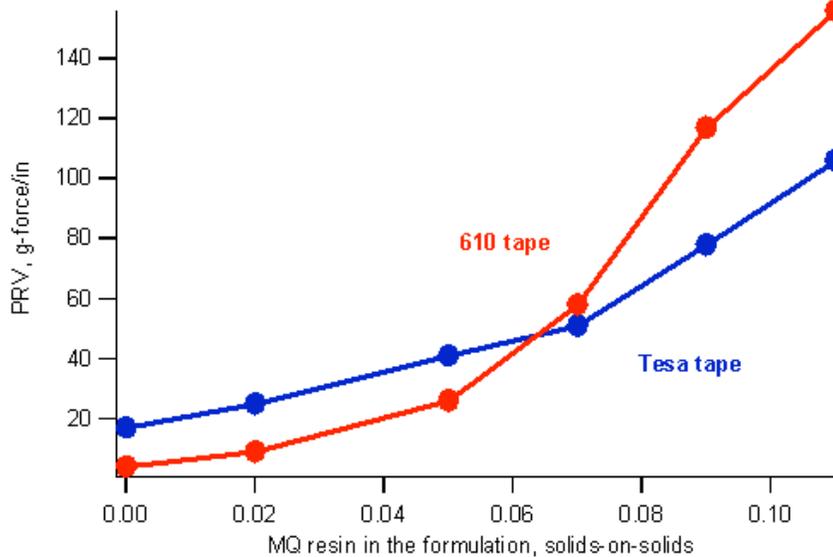


Figure 6. Effect of MQ resin on PRV of Coating 1

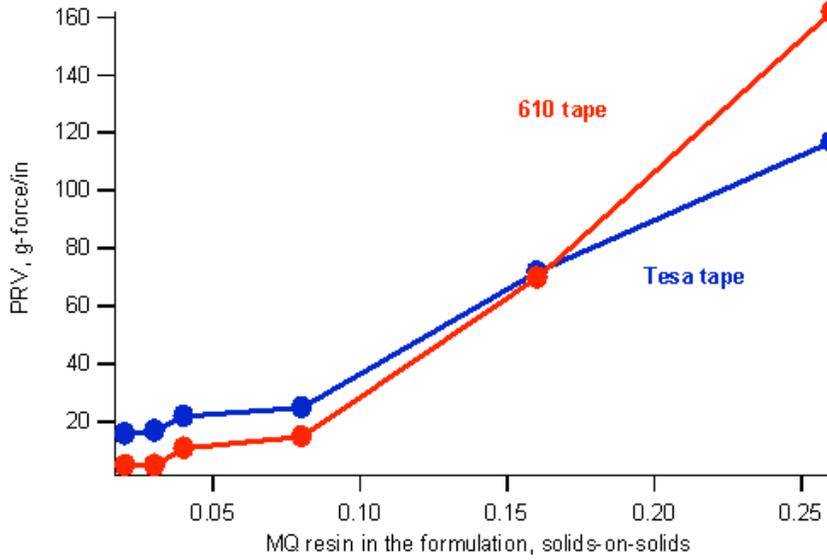


Figure 7. Effect of MQ resin on PRV of Coating 2

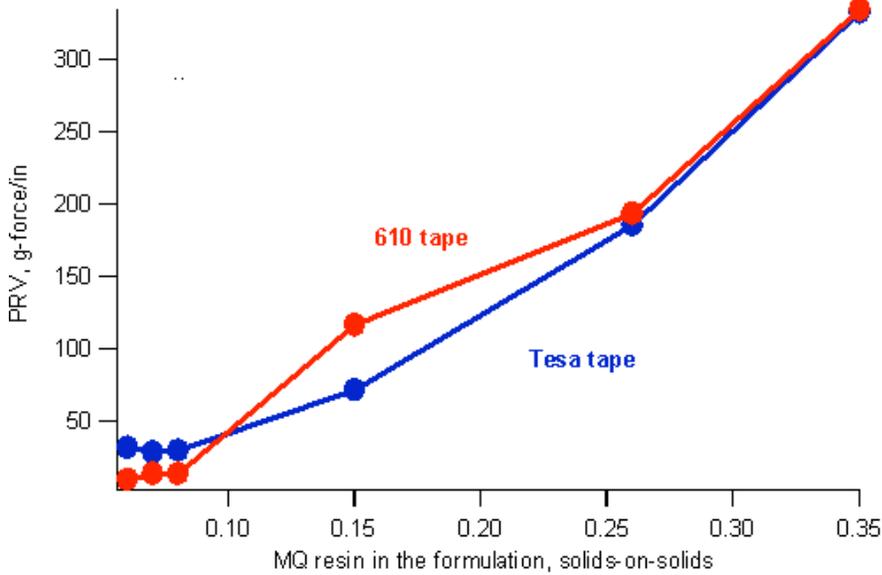


Figure 8. Effect of MQ resin on PRV of Coating 3

Dependencies presented in Figures 6-8 can be fit into one or another simple function. Figures 9,10 below present a fit of experimental PRV values against [MQ] using quadratic and exponential functions, respectively:

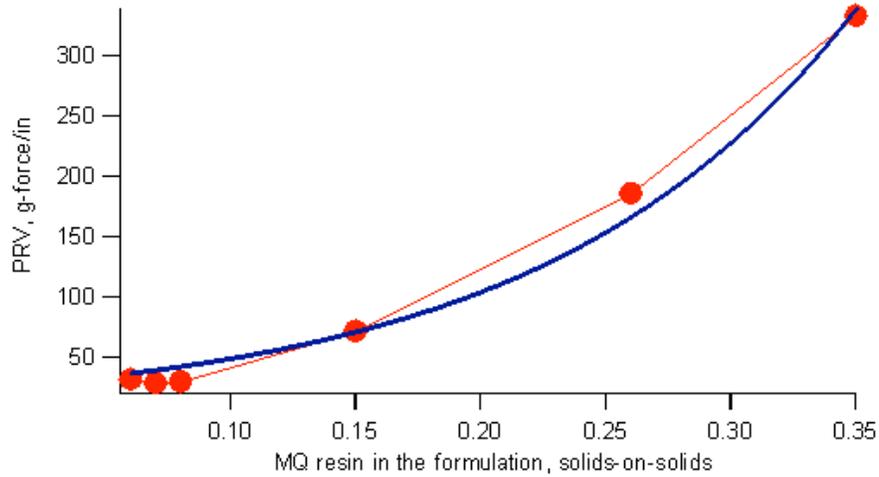


Figure 9. Effect of MQ resin concentration on PRV of Coating 3. Experimental data are for Tesa tape (Figure 8), a smooth line is a fit into quadratic function

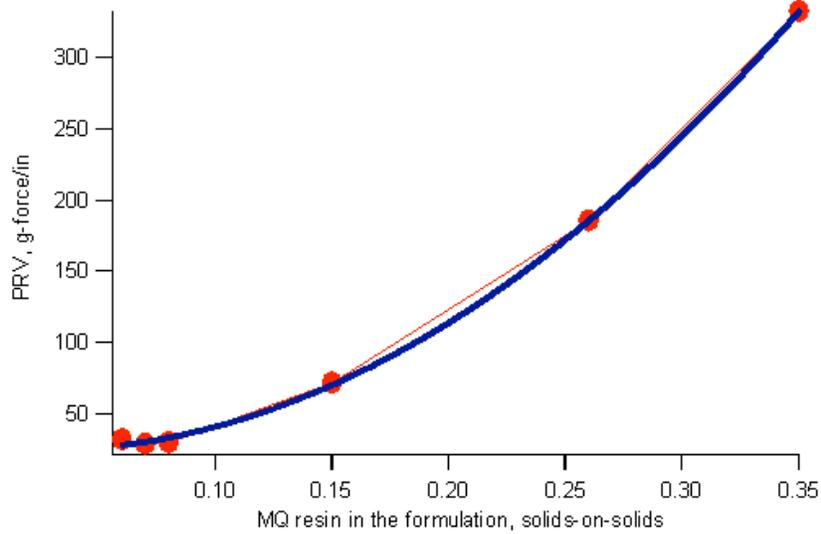


Figure 10. Effect of MQ resin on PRV of Coating 3. Experimental data are for Tesa tape (Figure 8), a smooth line is a fit to exponential function

Curves presented in Figures 6-8 demonstrate a strong dependence of PRV upon [CRA]. One can get a very high PRV with sufficient [CRA]. The curves allow prediction of PRV with sufficient accuracy for a formulation with constant concentrations of other components. These curves are close to being, but are not exactly, the same because of sensitivity of the PRV to batch-to-batch variation of the CRA and small variations in the ratios of other formulation components.

Liners covered with the cured Coatings 1-3 were laminated to a clear 1mil PET film using a commercially available acrylic pressure sensitive adhesive. The peel release value for removal of the liner film from the laminate is almost independent of the amount of CRA in the silicone formulation. Values of PRV of 4, 4 and 16 g-force/in were found for laminates with Coatings 1, 2, and 3, respectively. This data illustrates the difficulty of defining what the performance of a release liner is.

An important demand for a liner is the lowest possible transfer of silicone release coatings to the adhesive upon removal of the liner. We studied with X-ray photoelectron spectroscopy (XPS) the surface of an acrylic adhesive after removal of liners, Figure 11. The data is summarized in the Table 1. One can see from the data of Table 4 that addition of CRA to the formulation not only changes the PRV but also the amount of silicone transferred to the adhesive.

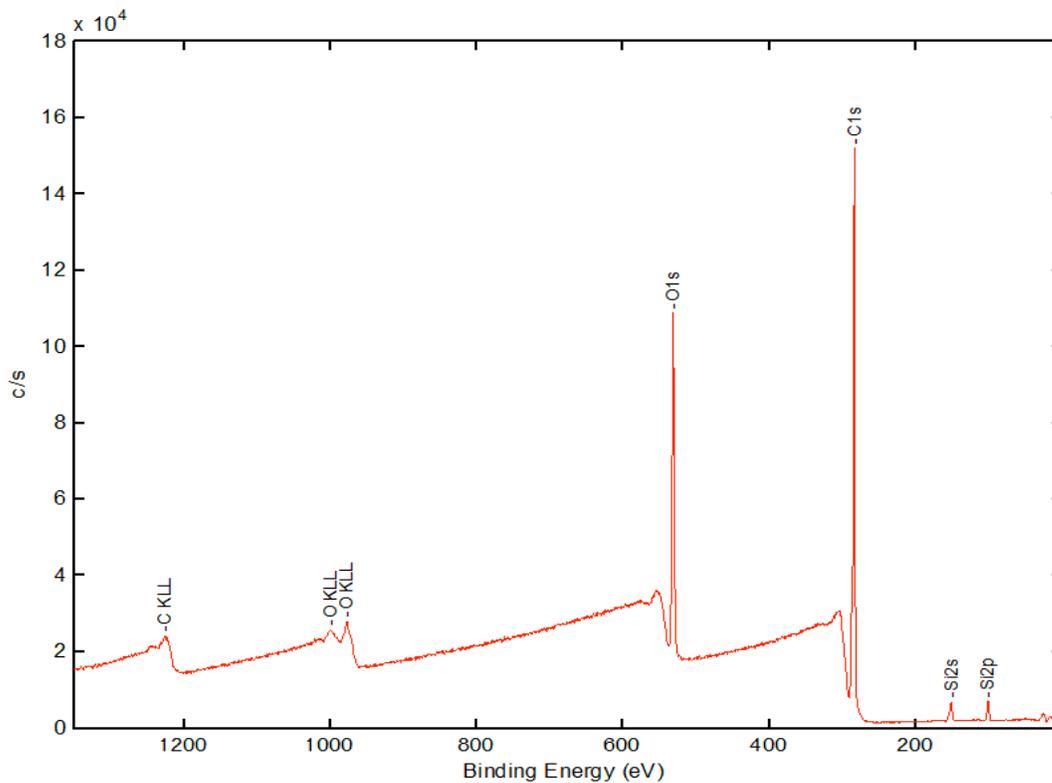


Figure 11. XPS spectrum of an adhesive surface after removal of release liner with Coating 1

Table 4 presents numerical values of atomic concentration of the surface of adhesive and a comparison of the amount of silicone present with a pure PDMS coating:

Table 4

**Atomic Concentrations<sup>a</sup>**

Sample	C	O	Si	%PDMS
Coating 1	76.5	21.2	2.4	9%
Coating 2	60.6	28.9	10.5	42%
Coating 3	56.8	30.7	12.5	50%
PDMS (theory)	50.0	25.0	25.0	100%

<sup>a</sup>Presented in %. Determination error is  $\pm 2\%$ .

Normalized to 100% of the elements detected.

XPS does not detect H or He.

## Conclusions

We have briefly considered some of the problems related to specification of peel release coatings and peel release liners. Because of the variability in measuring peel release values, determining whether one liner is equivalent to another is difficult. Errors in PRV measurement can be minimized by a few simple expedients and an understanding of the effect of a controlled release additive can be used to adjust PRV. However in doing so other characteristics of the release behavior can vary, for example transfer of silicone on release from the adhesive. Liners are used for a subsequent application of adhesive and a manufacturer of liners often is not aware of the nature of adhesive to be used with that liner. As we have seen, different adhesives do not simply produce an offset in PRV but can show a completely different dependence on added controlled release additive, for example.

Photopolymerization is a well established method for preparing liners. To be successful in replacing tin-based chemistries it will need to successfully negotiate all of the above concerns and more.

## References

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