Effect of Control Release Additives on Peel Release Values of Silicone Liners

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Abstract

Silicone release coatings have wide industrial applications from removable labels to displays, window films and other applications. We studied silicone release coatings on PET with a goal to be able to produce coatings with predictable peel release values (PRV). We studied in detail the effect of silicone control release additive (CRA) and found that not only does the PRV of a silicone liner depend upon the amount of additive used but that the effect of the CRA is also adhesive dependent.

Introduction

Most release coatings are silicones, usually crosslinked PDMS-type materials. Silicones dominate the market: they have excellent anti-stick properties. These properties originate from the low surface tension of silicones and flexibility of Si-O-Si bond. Industry uses test tapes to measure an important property of silicone release coatings or silicone liners, the peel release value (PRV). PRV is the force required to peel an adhesive from a release liner and is traditionally measured in g-force/in. SI equivalent units will be N/m or kg/s². Popular test tapes used in the industry are “Scotch® 3M 610” tape (“610” tape) and tesa® 7475 or 7476 tapes. In our experience, tesa® 7475 gives more reliable results with less scatter than “610” tape.

PRV strongly depends upon the geometry of a peel tester during measurements: the angle of peel, rate of peel, and the preparation and conditioning the sample. This will consist of a test tape or any adhesive coated film 1” wide adhered to the release liner.

Dehydrogenative condensation

Release coatings are produced by photo- or thermal polymerization. We deal in this presentation with coatings prepared by the latter method. We studied mainly raw materials and base formulations of thermal cure release coatings available from Momentive Performance Materials,® inc. (“Momentive") (Waterford, New York).

Liquid formulations of release coatings usually have a high concentration of hydrocarbon solvents. Solvents evaporate and are removed during cure. Solvent-borne formulations allow very thin release coatings to be deposited with a thickness less than 100 nm.
“Sn”-catalyzed thermal cure of siloxanes is a reaction between a silicone diol (α,ω-dihydroxy-terminated PDMS, silanol) and a relatively low molecular weight silicone with hydro- and methyl groups (silane). Cure is a dehydrogenative condensation:

\[
\begin{align*}
\text{Si-OH} + \text{Si-H} & \xrightarrow{\text{catalyst}} \text{Si-O-Si} + \text{H}_2 \\
\text{CH}_3 \text{SiH}_3 & \xrightarrow{\Delta} \text{CH}_3 \text{SiCH}_3 + \text{H}_2 \\
\end{align*}
\]

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 (~ 150 °C) once solvents have evaporated.

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 accelerate the bimolecular reaction (1).

**Experimental**

We studied in the present work different formulations prepared according to the manufacturer’s recommendations. The formulation named A was studied in detail as an exemplar.

We will discuss results obtained with tesa® 7475 tape below. Measurements of PRV were performed with a peel tester such as the IMASS SP-2000 or 2100 of IMASS inc. We used the following conditions: peel rate 90 in/min; the highest position of the tape grip above the moving platform, which is 1.75”, and sample length 10.0”. The fixed length is important for getting a reliable PRV.

We prepared three liquid formulations A, B and C which include silanol, silane, amino substituted silane, “Sn” (all of “Momentive”) and toluene/hexane mixture as solvent. We will label these formulations, which do not have a control release additive (CRA), as \( A_o, B_o, \text{ and } C_o \). \( A_o - C_o \) with some added CRA are denoted as A-C, respectively. Formulations \( A_o - C_o \) have slight differences in relative concentration of components.
Cure of all formulations studied in this work was performed in a convection oven at 149 °C (300 °F) for 60 s. Thickness of the coating was measured by an Oxford 3000 XRF instrument. All coatings were 100 ± 20 nm thick. Coatings were applied to 1 mil PET film of Toray.

Release liners, like most quickly cured coatings, undergo post-polymerization for at least several days.\textsuperscript{5,6} We applied a test tape to five-days-old cured coatings with a 4.5 lb calibrated hand rubber roller, 1 h prior to PRV measurement with the IMASS.

Liners covered with cured coatings A-B were laminated to a clear 1mil PET film U65 using commercially available acrylic pressure sensitive adhesives, abbreviated here as adhesives 1 and 2. Release liner was removed from a laminate the same way as a test tape, and PRV was measured.

**Results and Discussion**

After curing, starting formulations A\textsubscript{o}-C\textsubscript{o} demonstrate relatively low PRV of 20-30g-force/in. It is necessary to add CRA to get a higher PRV. We used “Momentive” MQ resin as the CRA. MQ resin is a copolymer of monofunctional silicone unit M with tetrafunctional unit Q.\textsuperscript{4} An approximate composition of MQ resin is 15 M: 25 Q: 3 Si-OH. MQ consists of ~ 40 Si atoms total and is obtained by the hydrolysis of trimethylchlorosilane in aqueous sodium silicate. The exact dimensions, $M_w$, structure, and reactivity of MQ resin varies depending upon hydrolysis conditions.

Figures 1 demonstrates the effect of MQ resin upon formulation A\textsubscript{o}:

![Figure 1. Effect of MQ resin on PRV of a silicone coating A](image)
Figure 1 presents a strong dependence of PRV upon [MQ]. We fit the data into a linear plot which turns out to be quite satisfactory. The linear plots allow prediction of PRV with sufficient accuracy to be useful when the concentrations of other components are constant. Rather similar linear plots of PRV vs. [MQ] were seen for other formulations, which had slightly different ratios of components, cf. Figure 2:

These plots are close to each other, and errors in measuring PRV would mask small differences. The RMS errors of the individual data sets A-C and the combined data are little different.

One can get a very high PRV with sufficient [MQ]. It is expected that when MQ is the main component of a formulation on solids, one will get a coating rather more like a pressure sensitive silicone adhesive.

PRV for removal of the silicone liner from the laminate depends both on the amount of CRA in the silicone formulation and the adhesive in the laminate, Table 1.
Table 1

PRV of separation of release liner from laminates with a tape and with two acrylic pressure sensitive adhesives*

<table>
<thead>
<tr>
<th>MQ resin solids-on-solids</th>
<th>PRV vs. tesa® tape</th>
<th>PRV vs. adhesive 1</th>
<th>PRV vs. adhesive 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>25 (12%)</td>
<td>6 (19%)</td>
<td>6 (8%)</td>
</tr>
<tr>
<td>8%</td>
<td>100 (10%)</td>
<td>6 (12%)</td>
<td>12 (14%)</td>
</tr>
<tr>
<td>15%</td>
<td>125 (9%)</td>
<td>16 (7%)</td>
<td>26 (3%)</td>
</tr>
</tbody>
</table>

*PRV values are in g-force/in. The value in parenthesis below PRV value is its determination error.

The data of Table 1 illustrates the difficulty of defining what the performance of a release liner is. The adhesive used on the tesa® tape clearly behaves differently from adhesives 1 and 2. Furthermore while with adhesives 1 and 2 the effect of CRA is not large and a range in PRV of 6-26 g-force/in would be acceptable in many applications, the difference between adhesive 1 and 2 may be critical for differential release applications. The adhesive used on the test tape would clearly be amenable to differential release applications. Unfortunately the present level of adhesion science and technology does not make it possible to predict PRV of a particular silicone-adhesive pair and we rely on observed empirical correlations like Figure 1 to have some predictive power.

It is important that release liners do not undergo much aging and have a shelf life of 12 months.
Figure 3. Dependence of PRV for the three cured liners during storage under ambient conditions. A₀ has no CRA, B has 8%, C has 15% of CRA (solids-on-solids).

Figure 3 demonstrates lack of obvious dependence of PRV vs. time because of the determination errors in measuring PRV, which is good from a end-user standpoint.

Conclusions

We have briefly considered some of the problems related to specification of peel release coatings and peel release liners and laminates. Because of the variability in measuring PRV, 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. 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 show different PRV with the same liner and can also show a completely different dependence on added controlled release additive, for example. Optimization of PRV by addition of control release additive (CRA) should be done with each of the selected adhesives because effect of CRA on PRV is adhesive dependent.

References

3. [http://www2.momentive.com/ProductFamily/Silicones.aspx](http://www2.momentive.com/ProductFamily/Silicones.aspx)

