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# Recrystallization of silicone release coatings

**E. P. Chang**

Avery Dennison, Pasadena Laboratories, 2900 Bradley Street, Pasadena, CA 91107, USA

## Summary

The degrees of recrystallizability of silicone release coatings with different crosslink densities have been determined via monitoring the recrystallization peak of the temperature scan on the Rheometrics-RMS-800 Spectrometer and DSC. As the crosslink density of the release coating increases, the recrystallization peak of silicone diminishes sharply indicative of the increasing constrains imposed by the high crosslink density which reduces the recrystallizability of the silicone. In addition, Tg of the silicone also increases, together with a lower recrystallization and melting temperatures.

## Introduction

Crosslink density in silicone release coating has important consequences on both the release as well as as adhesion performance of pressure-sensitive adhesive constructions (1). Crosslink density has different definitions. From the chemistry point of view, it is a measure of how much of the vinyl groups has reacted with the silicon hydride, the crosslinker. It can be also defined as how much unreacted (extractible) material is present after the cure. From the rheology point of view it is a measure of how high is the plateau modulus, which is inversely related to the molecular weight between crosslinks.

Polydimethylsiloxane is a semicrystalline polymer with a sub-ambient melting point (2-6). At room temperature, crosslinked silicone is a clear rubbery solid containing melted crystallites embedded in a crosslinked network. The crystallizability of a silicone network is inversely proportional to its crosslink density. In other words, the more crosslinked is the silicone, the more restrictive its molecular mobility, hence, the less tendency for it to crystallize. The objectives of this paper are:

- To correlate crosslink density from a different perspective of chain mobility or recrystallizability.
- To demonstrate the enormous sensitivity of the recrystallization peak as observed from the temperature scan by Rheometrics or DSC.
- To demonstrate how this different degree of crosslink density or crystallizability affects silicone's Tg, Tm, and plateau modulus.

## Experimental

All the silicone formulations are derived from a General Electric-solventless SL-5000 release coating system. It consists of a vinyl-terminated polydimethylsiloxane with a platinium catalyst (SL-5010), base polymer without catalyst (SL-5000), an inhibitor to prevent crosslinking at room temperature (SL-5040), and a crosslinker composed of methylhydropolysiloxanes (4330-C). For clarity, only three samples representative of a well-cured, a medium-cured and an undercured sample are reported.

### 1).Sample Preparation

The compositions and cure conditions for the samples investigated are listed in Table I. The mixing procedure is as follows:
Weighed amounts of the base polymer without catalyst (SL-5000), the base polymer with catalyst (SL-5010), and the inhibitor (SL-5040) were first mixed thoroughly for three minutes, followed by the last addition of the crosslinker. The formulation was then stirred again for another two minutes to ensure good mixing and allowing entrapped air to escape.

### 2).Conditions of Measurements on the Rheometrics

The liquid silicone sample was introduced between the parallel plates with a gap of about 1.0 to 2.0 mm on a Rheometrics-RMS-800 spectrometer.The in-situ curing studies were carried out isothermally at the desirable cure temperatures for 20 minutes in nitrogen using 8 mm plates. Dynamic storage shear modulus G', dynamic loss shear modulus G", and tan ∂ values were measured every 0.2 minute at a frequency of 10 rad/s. The strain employed was about 3%.

Immediately after the cure cycle, the cured sample is quenched to about -150 ° C in the rheometer. Care was taken to ensure that the quenching rates for all the samples were approximately the same. A temperature scan from -150 to 150 ° C was then carried out at 3 ° C per measurement at a frequency of 10 rad/s.

### 3).Conditions of Measurements on the DSC

Cured samples were quenched to -150 ° C on a DuPont TA-2100-930 dual sample cell DSC, and scanned at a heating rate of 20 ° C/min. Sample size was about 10 mg. Tg was determined at the point of inflection (or peak of the derivative) of the endothermic displacement, while recrystallization and melting temperatures were taken at peak positions.

## Results and Discussion

### 1.Temperature Dependence of G'

### 1.a.The Glass-Transition and Crystallization Regions

Figure 1 compares the temperature dependence of G' from -150 to 150 ° C. for samples A, B and C. It can be observed that around -110 ° C, there is a precipitous drop in G' values indicative of the glass transition of silicone. Immediately above Tg, there is an upswing in G' for all the samples. For sample A which is the under-cured sample, there is a more than 3 decade increase in G' indicative of the highest degree of recrystallization. The medium-cured sample B showed a 1.5 decade increase in G', indicative of a lower but still substantial recrystallization of the silicone network. The well-cured sample, showed only a very slight increase in G' indicative of the relative lack of recrystallization. The areas under the recrystallization peak have been measured (ratio of 220, 59 and 11) and are directly proportional to the degrees of recrystallization for these quenched release coatings.

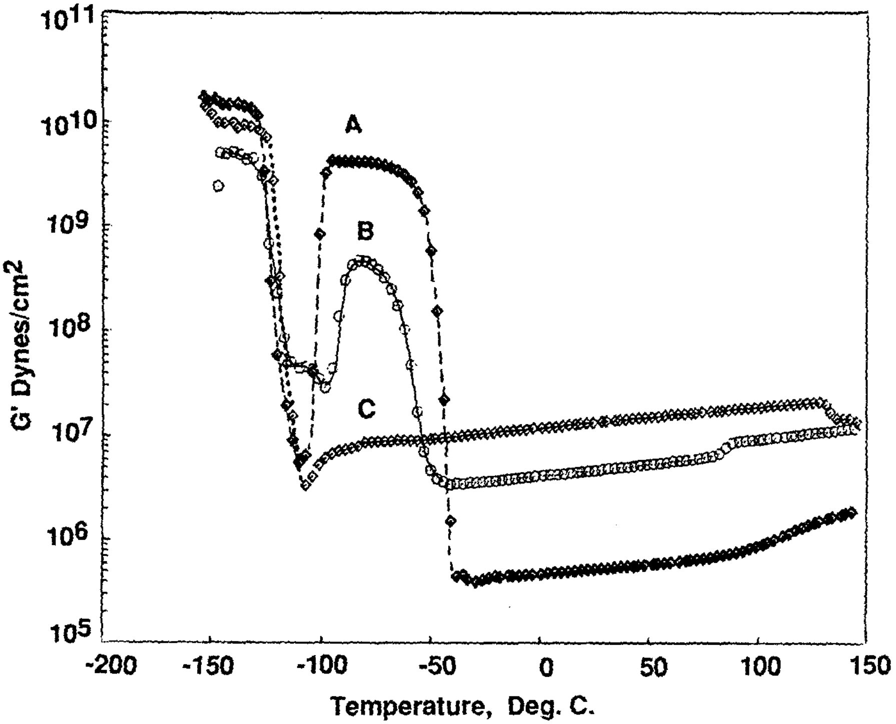


**Figure 1: Temperature Dependence of G' for release coating samples with different levels of cure.**

### I.b.The Melting Transition Region

Immediately after the recrystallization peak, there is again a second drop in G' values attributable to the melting transition of the silicone crystalline phase.The drop in G', as well as their onset of melting temperatures are very sensitive to the degree of cure of the sample. For the under-cured sample A, there is an about four- decade drop in G' and the onset of melting temperature is high, indicative of the highest crystallinity and crystal perfection. The medium-cured sample B, shows a moderate two-decade drop in G' values indicative of medium crystallinity and crystal perfection. The well-cured sample C, shows hardly any drop in G' indicative of very low amount of very imperfect crystallites.

### I.c.The Rubbery Plateau Region

Immediately after the melting, there is a region where the modulus stays fairly constant. This region, which is rather temperature insensitive, is the rubbery-plateau region. For these three samples, the onset temperatures of their plateau regions also vary significantly with their different degrees of cure. For sample C, which is the best cured, this occurs at -80 ° C. For sample B, which is medium cured, plateau region onsets at about -50 ° C. For sample A, which is under-cured, this does not occur until all the crystallites have melted and thus occurs at about -35 deg.C. The plateau moduli ( G' values measured at 23 ° C) of these samples are also quite different, with $5 \times 10^5$, $5 \times 10^6$ and $1.5 \times 10^7$ dynes/cm$^2$, respectively, for samples A, B and C. Approximate average molecular weights between crosslinks using a simplified rubber elasticity equation by Tobolsky et al. (7) ; $Gn \simeq \rho RT / M_c$, are 65000, 6500, 2200 respectively. Gn is the plateau modulus, ρ is the density $\simeq 1$, R is the gas constant, T is the absolute temperature and $M_c$ is the molecular weight between crosslinks.

## 2. Temperature Dependence of tan δ

### 2.a.The Glass-Transition and Recrystallization Regions

Figure 2 shows the corresponding temperature dependence of tan δ for the three samples from -150 to 150 ° C. Figure 2(a) shows the expanded plot of Figure 2 from temperature of -150 to 0 ° C., to magnify the transitions as indicated by tan δ maxima. From -130 to -90 ° C., the under-cured sample A shows a major Tg peak at about -123 ° C with a shoulder at -116 ° C. assigned to the recrystallization. The medium cured B sample, shows three transition peaks, -123, -116 and -96 ° C. The triplet suggests that the chemical environment is heterogeneous. It is noteworthy that this sample has a low amount of crosslinker and the lowest catalyst content, hence might contain heterogeneous regions of low and high crosslink densities, giving rise to the two Tg peaks at -123 and -116 ° C respectively.The -96 ° C peak is attributed to recrystallization. The well-cured sample C, shows one predominantly Tg peak at about -116 ° C, with a rather indistinct shoulder at about -110 ° C. The rather sharp and high tan δ maximum of this sample indicates high amounts of amorphous (or non-crystalline) content and a rather homogeneous crosslinked environment yielding a high crosslink density, and hence a high Tg.

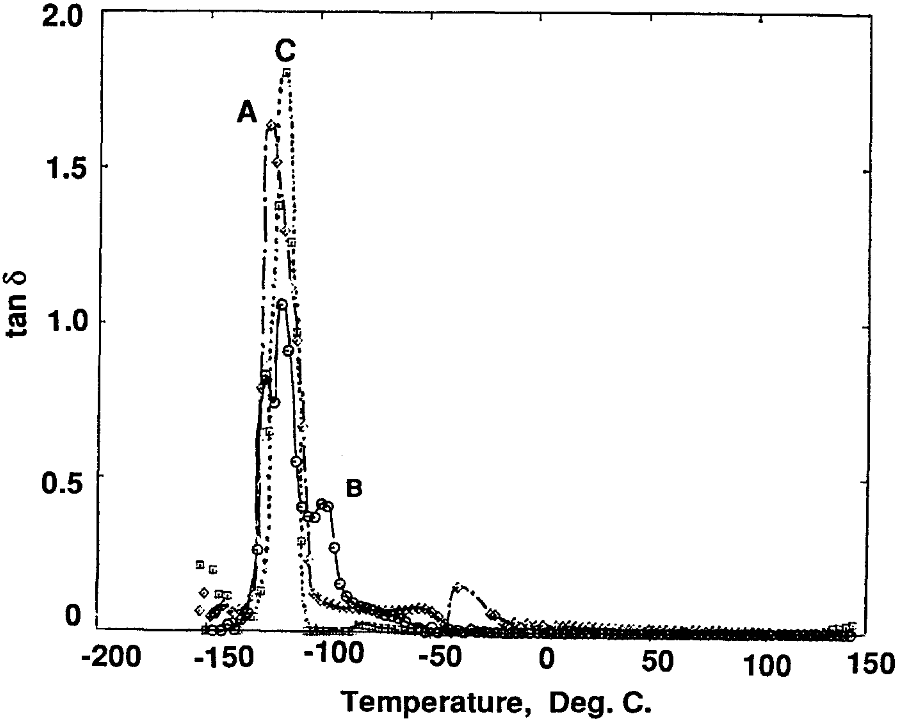


Figure 2: Temperature Dependence (from -200 to 150 deg. C) of tan ∂ for release coating samples with different levels of cure.

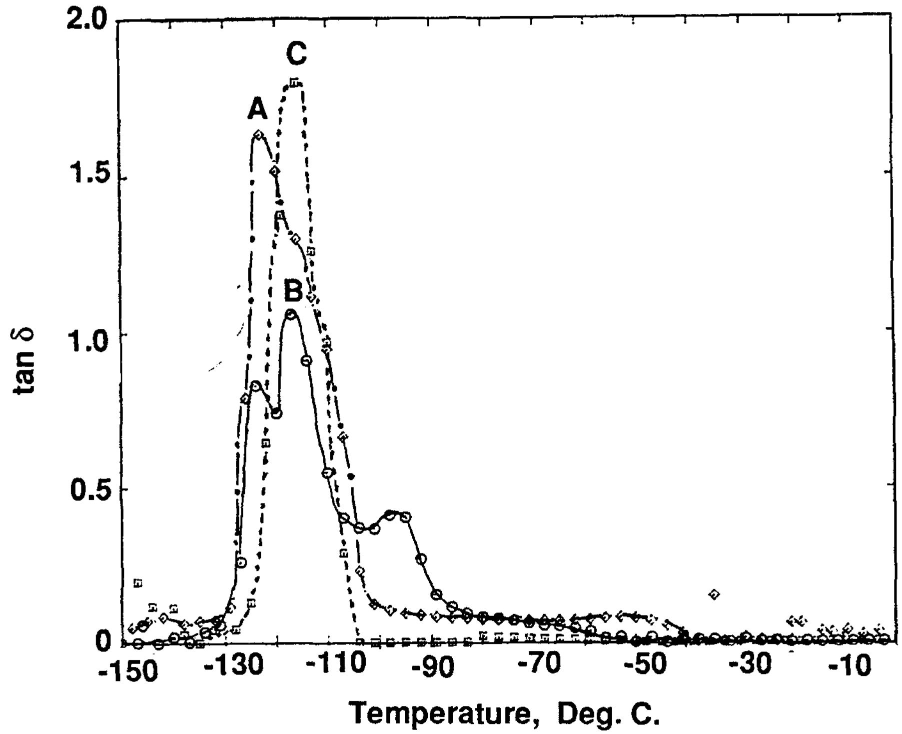


**Figure 2(a): Expanded Temperature Scale from -150 to 0 deg. C. from Figure 2. to magnify the Tg transitions**

Figure 2(b) shows the blow-up plot of Figure 2 from -90 to -40 ° C, to magnify the melting transition. The under-cured sample A shows the highest melting temperature of about -50 ° C, indicative of the highest crystallinity and the highest melting temperature. The medium-cured sample shows a fairly broad Tm centering at about -65 ° C. The well-cured sample C, shows a rather indistinct Tm of about -80 °C . The different Tm's of these samples can be attributed to their respectively degrees of crystallinity and different degrees of crystallite perfection. For a well-cured silicone network with a high crosslink density, crystallization is difficult, because of the limited mobility of the polymer chain. Hence, any crystallites would be rather imperfect and will have a low melting temperature. The under-cured sample A, with a low crosslink density is expected to be more crystallizable because of the relative ease of molecular motion. Therefore, higher crystallinity together with better developed crystallites and a higher Tm would be expected.

Table I shows the characterization of the three samples by gel content and swell ratio. Table II shows rheological highlights. Comparing the two tables, it can be observed that there are fairly good correlations among the crosslink densities determined by different test methods. i.e. lower swell ratio, and higher gel content can be correlated with lower crystallizability obtained in this study. However, it is apparent that the quenching / recrystallization technique is much more sensitive, hence will make samples with small cure level differences more distinguishable.

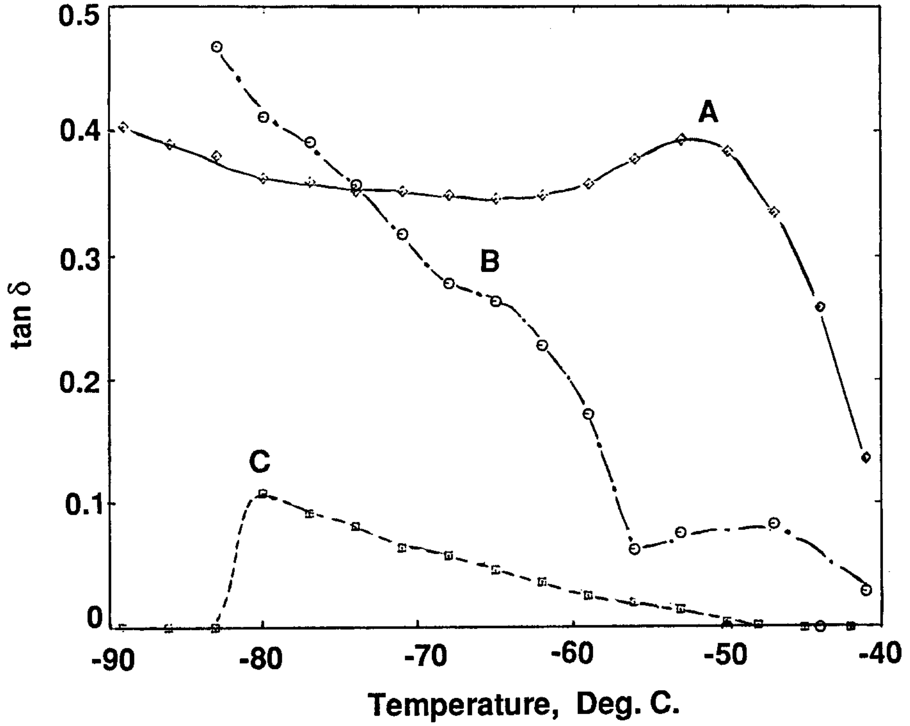


Figure 2(b): Expanded Temperature Scale from -90 to 40 deg. C. from Figure 2 to magnify the Tm transitions.

Table I

Composition, Cure Condition and Gel Analysis of Samples A, B and C

| Sample | SL-5000,g | SL-5010,g | SL-5040,g | SS-4300C,g | Cure Temp | Gel Content | Swell Ratio |
|---|---|---|---|---|---|---|---|
| A | 48 | 52 | 1.04 | 3 | 90° C | 61.2% | 8.5 |
| B | 82.5 | 17.5 | 0.35 | 3 | 110° C | 97.3% | 4.8 |
| C | 6 | 94 | 1.86 | 10 | 110° C | 98.7% | 5.0 |

Table 2

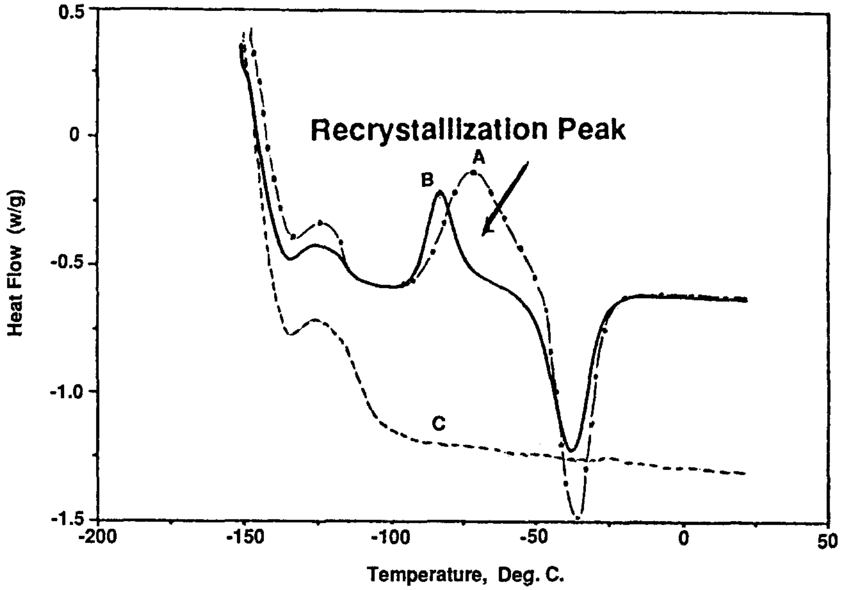
Comparison of rheological features for samples A,B, and C from the recrystallization study

| Sample | Recryst.Peak from G',Area | Melting Peak, ° C | Onset Temp. of Plateau, ° C | G' at 25°C (Dynes/cm2) | Tg,TcPeaks from tanδ maximum, ° C |
|---|---|---|---|---|---|
| A | 220 | -50 | -40 | 5x $10^5$ | -123(Tg), -116 (Tc) |
| B | 59 | -65 | -45 | 5x $10^6$ | -123(Tg), -116 (Tg), -96(Tc) |
| C | 11 | -80 | -60 | 1.5x$10^7$ | -116 (Tg),-110(Tc) |

Tc= Recrystallization Temperature

## 3.Confirmatory Analysis by DSC

To confirm the recrystallization behavior of these samples, confirmatory DSC experiments were carried out . Figures 3 compares the thermograms of the same series of bulk-cured samples after quenching to -150 ° C. The under-cured sample A shows the lowest Tg, largest heats of recrystallization and melting, with highest recrystallization and melting temperatures. The well-cured sample C, shows the highest Tg, with no detectable recrystallization. The very weak crystallization by DSC versus a very small recrystallization peak by Rheometrics can be attributed probably to the higher sensitivity of the dynamic mechanical measurements, the different quenching rates in the two instruments and different forms of samples. Nevertheless, the two types of measurements are in excellent agreement, indicating that both methods can be used for monitoring the cure levels in silicone release coatings.



**Figures 3: DSC thermograms showing the different glass transition, recrystallization, melting transition temperatures and heats of recrystallization and melting for silicone samples with different levels of cure. (A) under-cured sample (B) medium-cured sample and (C) well-cured sample .**

Table III summarizes the thermal analysis data for the three samples, while Table IV compares the different physical properties of silicone coatings with a low versus a high crosslink density.

Table 3

Comparison of thermogram features for samples A,B, and C from the recrystallization study on the DSC.

| Sample | Tg °C | Recryst. Peak, ° C | Heat of Recryst. cal/g. | Melting Peak, ° C | Heat of Fusion cal/g. |
|---|---|---|---|---|---|
| A | -117.8 | -72.8 | 32.2 | -36.5 | 36.3 |
| B | -115.3 | -83.2 | 13.9 | -37.8 | 28.8 |
| C | -111.4 | --------------- not-detectable --------------- | | | |

Table 4

COMPARISON OF PROPERTIES OF A LOW VERSUS HIGH CROSSLINK DENSITY SILICONE RELEASE COATING

| | Low Crosslink Density | High Crosslink Density |
|---|---|---|
| MODULUS | LOWER | HIGHER |
| Mc | HIGHER | LOWER |
| CHAIN MOBILITY | HIGHER | LOWER |
| RECRYSTALLIZABILITY | HIGHER | LOWER |
| Tg | LOWER | HIGHER |
| Tm | HIGHER | LOWER |
| GEL CONTENT | LOWER | HIGHER |
| SWELL RATIO | HIGHER | LOWER |

## Conclusion

The degrees of recrystallizability of silicone formulations cured at different levels have been determined via monitoring the recrystallization peak of the temperature scan by Rheometrics and DSC. As the cure level of the release coating increases, the recrystallization peak sharply diminishes indicative of the increasing constrains imposed by the high crosslink density which reduces the recrystallizability of the silicone release coatings. In addition, Tg of the silicone also increases, together with a lower recrystallization and melting temperatures. This technique defines and determines crosslink density from a different viewpoint of chain mobility or recrystallizability.

## Acknowledgement

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