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Title: Solid Silicone Elastomer Material(DC745U)-Historical Overview and New Experimental Results

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Solid Silicone Elastomer Material (DC745U)-Historical Overview and New Experimental Results

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C-CDE: Chemical and Diagnostic Engineering Group

August 21st, 2012

Conversion Seminar

LA-UR-

Outline

- **Goal**
- **Introduction to DC745U**
- **Historical Review of DC745U experimental results (LA-UR-12-23612 and W-1-TR-0098U)**
- **Specific gaps**
- **Objectives**
- **New experimental data**
  - Post-cure Study
  - Low Temperature Mechanical Behavior
- **Summary and Conclusions**
- **Acknowledgments**

Goal

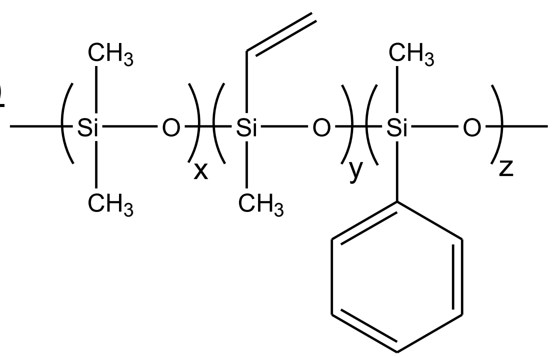
Material	Component	System Integration
Modeling: ▪Molecular Dynamics ▪Material Model	**Modeling:** ▪Constituitive ▪Uniaxial Compression	**Modeling:** ▪Thermomechanical ▪Hydrodynamic
Characterization: ▪Chemical ▪Physical ▪Thermal ▪Some Mechanical	**Characterization:** ▪Point Load ▪Density ▪Part Weight ▪Stability ▪Mechanical	**Characterization:** ▪Load Bearing Properties ▪Load Retention ▪Compression Set ▪Compatibility ▪Long-Term Stability ▪Lifetime Prediction

This presentation will focus on the material aspects of DC745U.

Introduction

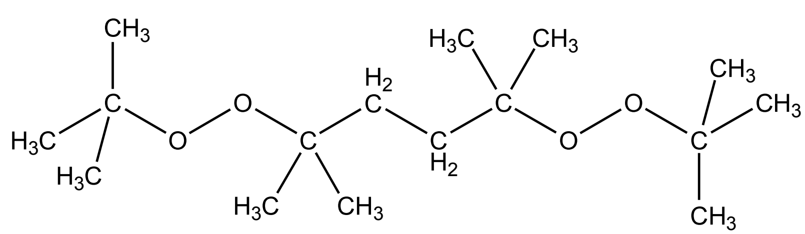
- **DC745U is a silicone elastomer used in several weapon systems.**
  - DC745U is manufactured by Dow Corning and its formulation is proprietary.
  - Risk- changes without notification to the customer.
- **^{1}H and $^{29}Si\{^{1}H\}$ NMR have previously determined that DC745U contains ~ 98.5% dimethyl siloxane, ~1.5% methyl-phenyl siloxane, and a small amount (<1%) of vinyl siloxane repeat units that are converted to crosslinking sites. The polymer is filled with ~ 38 wt.% of a mixture of fumed silica and quartz.**

Polysiloxane (99.5%)



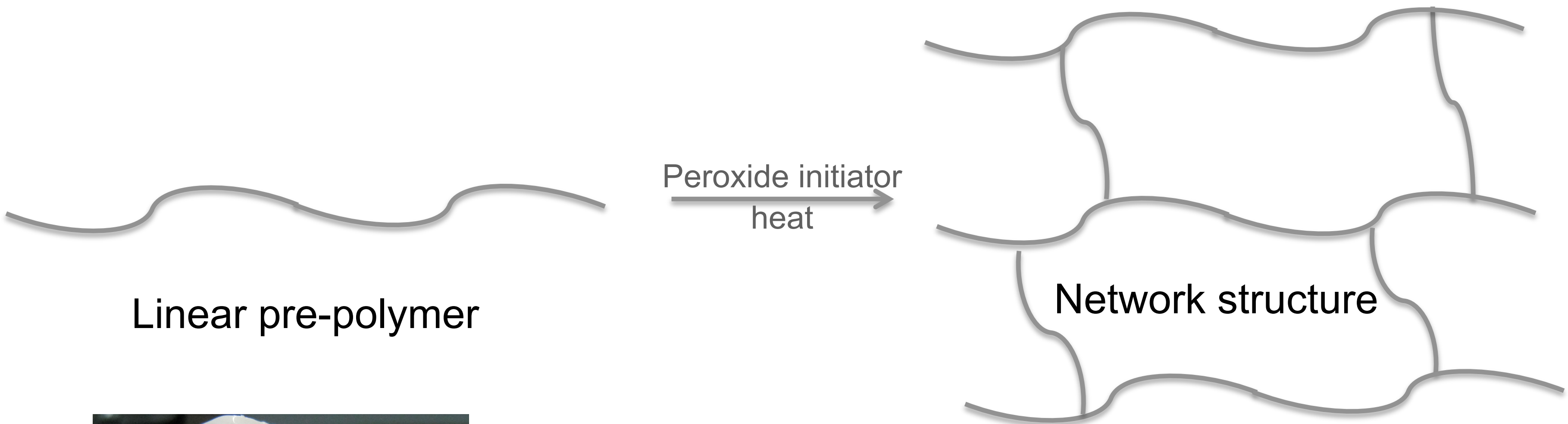
x = dimethyl siloxane monomer repeat unit (approx 98.5%)
y = methyl vinyl siloxane (approx 1%)
z = methyl phenyl siloxane (approx 1.5%)

Peroxide Curing Agent (0.5%)



Chemical Name: 2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane
CAS No. 78-63-7
Synonyms: Varox DBPH; Luperox101
Molecular Formula: $C_{16}H_{34}O_4$
Formula Weight: 290.44 g/mol

Reaction Scheme



Formulation, curing conditions, heterogeneities, and production process will determine the crosslink density, and thus the properties of the final product.

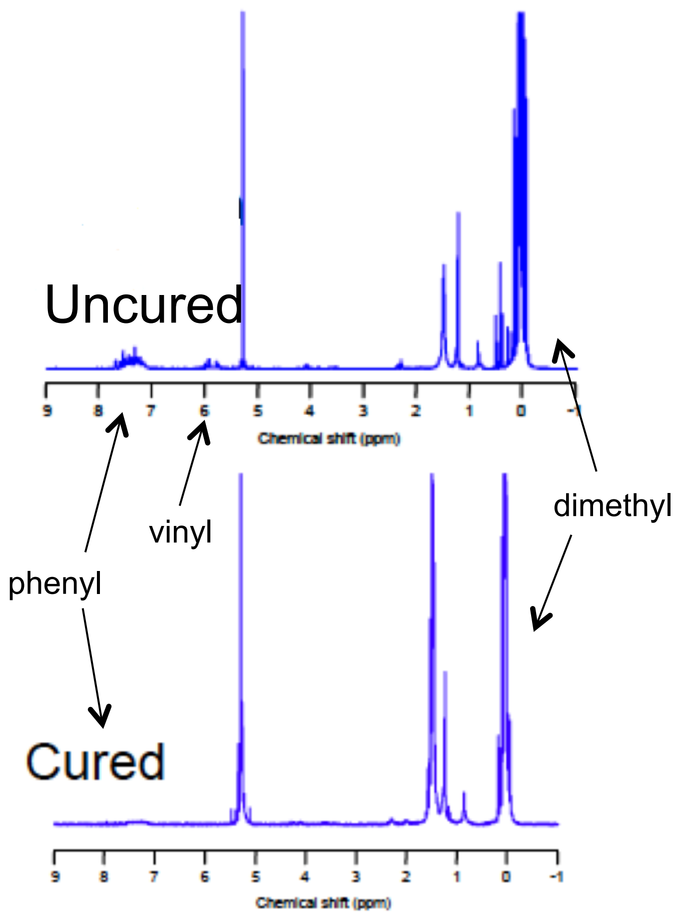
General Production Procedure of DC745U

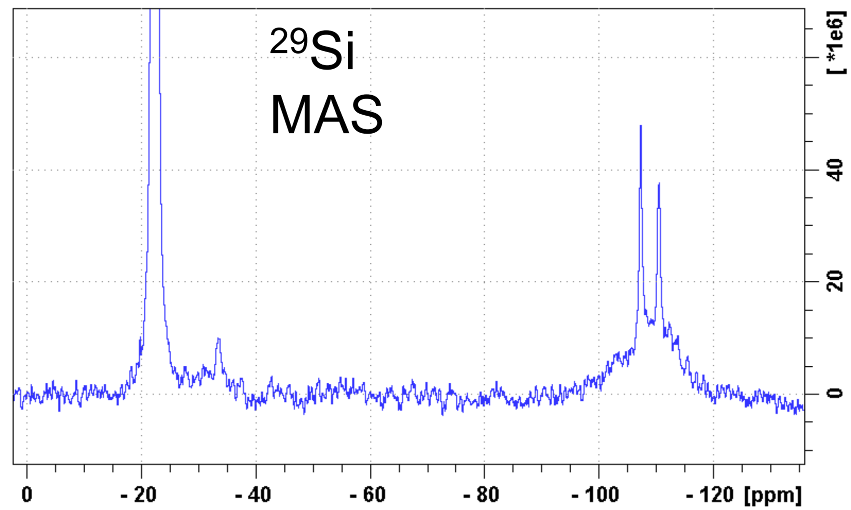
- **DC745U is mold cured at Honeywell's Kansas City Plant.**
- **The DC745U pre-polymer is passed through roll mills while the peroxide is poured in small quantities.**
- **The process is repeated until all initiator has been added.**
- **Circular preforms are cut and stacked, then placed in the mold, compressed, and degassed.**

- **The material is cured in the mold at 160 ºC for 1 hr.**
- **The molded part is post-cured in ovens at 149 ºC for 1 hr 15 min and at 249 ºC for 8 hr 30 min.**
- **The cured material density has been measured by KCP, LANL, and LLNL and is ~ 1.3-1.35 g/cm^3.**

Historical Material Analysis- Cured and Post-cured DC745U

- **NMR Spectra on extracts (LLNL)**
- **Solid state NMR of cured sample (LANL)**

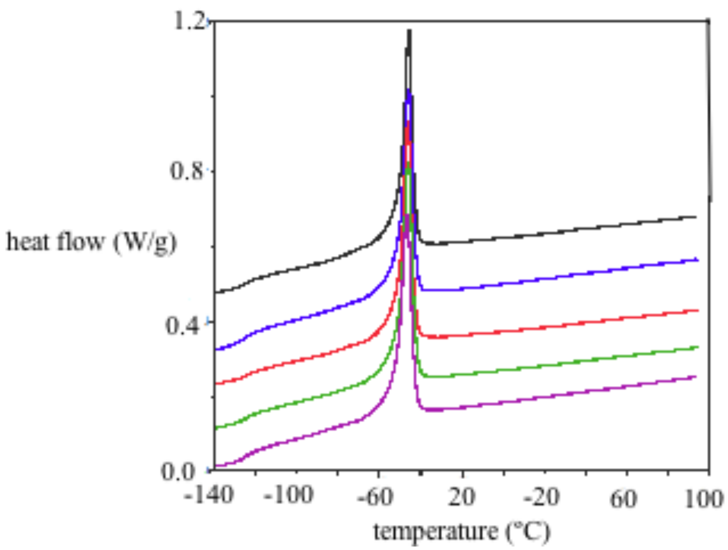




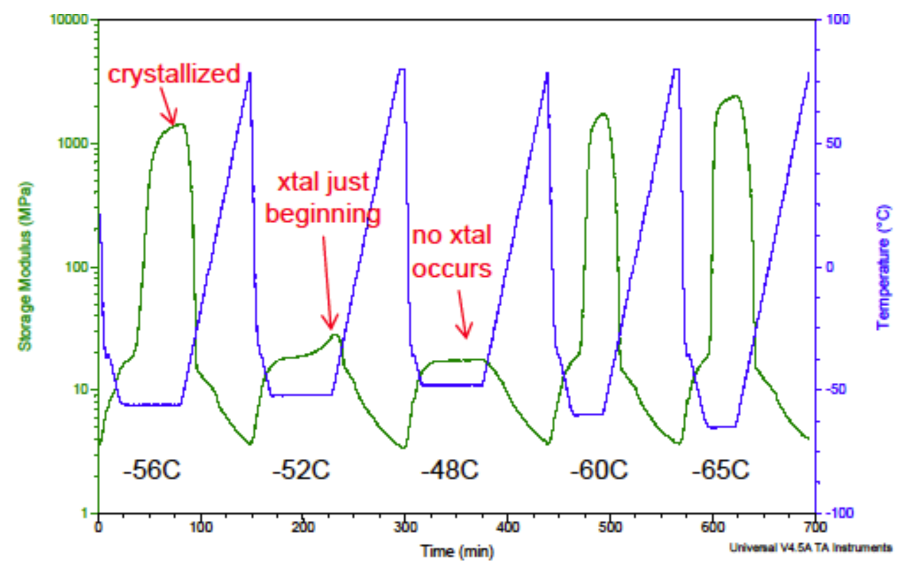
^{29}Si MAS-NMR for cured sample shows peaks at:
-35 ppm phenyl groups
-22 ppm dimethyl groups
-100 ppm silicate
-115 ppm quartz

Thermal Properties of DC745U

DSC



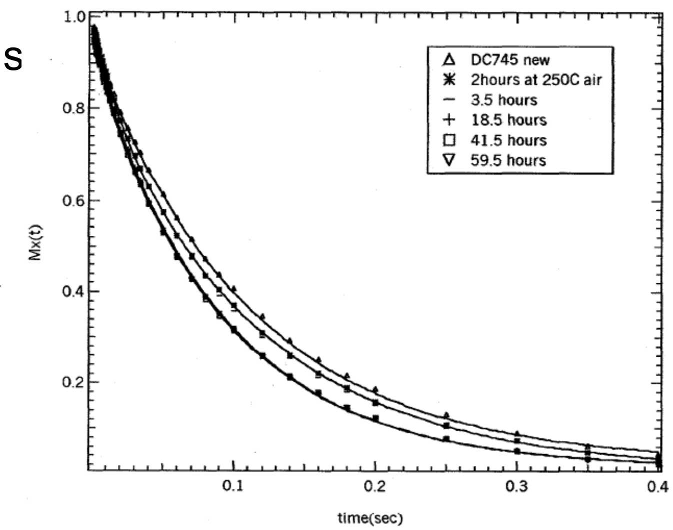
DMA



- Crystallization between -46 ºC and -56 ºC
- Crystallization impact on storage modulus at -52 ºC or lower temperatures.

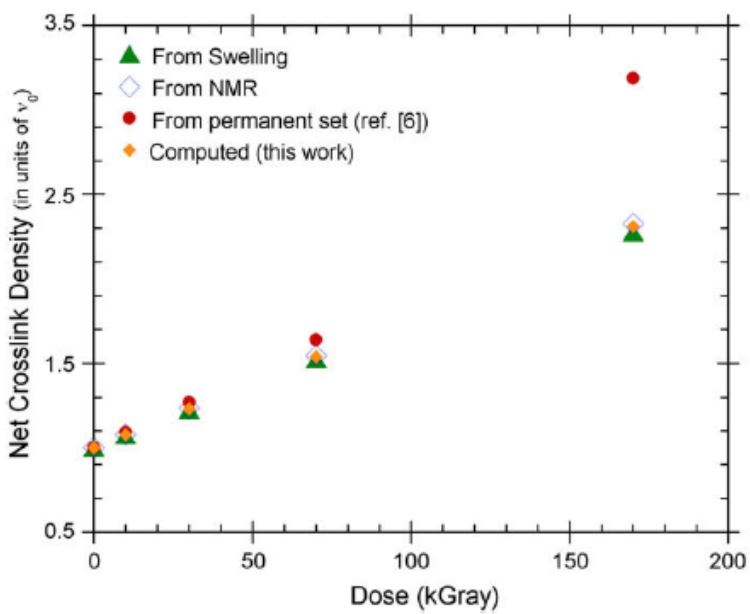
Historical Material Analysis- Thermal Aging

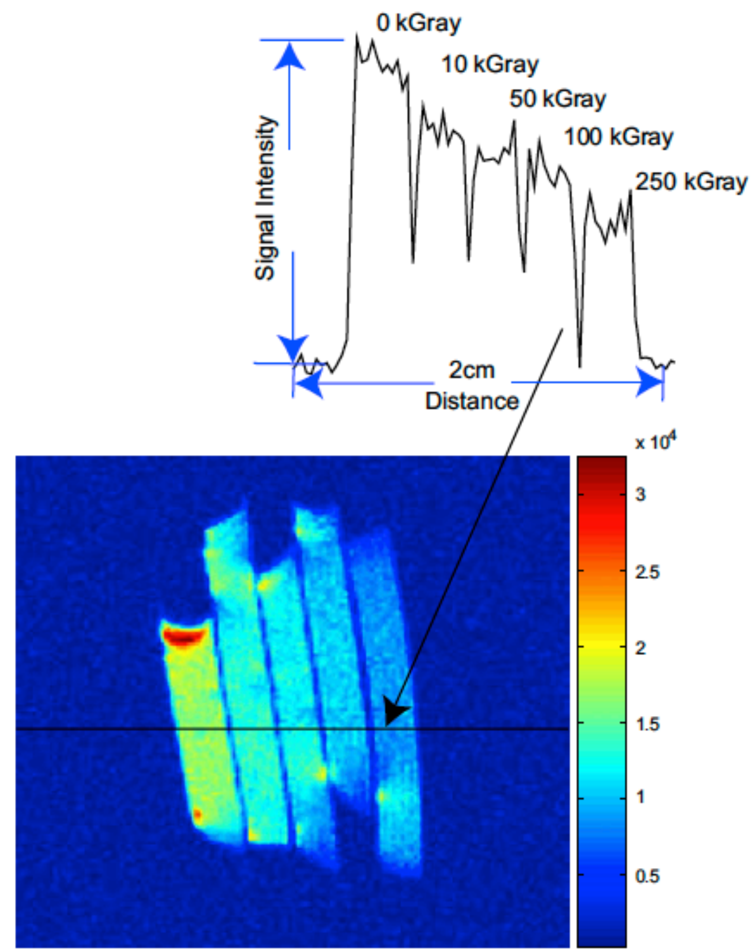
- **LLNL**
  - Conducted solid phase micro extraction (SPME) coupled with GCMS on samples that were heated at 70 ºC for 2 weeks.
  - Primary degradation products were linear and cyclic siloxanes.
- **LANL**
  - Conducted compression set studies at 80 ºC and 120 ºC for 6 months. Higher compression set (~ 100%) was observed for samples heated under compression at 120 ºC.
  - LANL heated the samples at 250 ºC for various time.
    - Longer time at 250 ºC = shorter T_2
    - Material is getting stiffer.
    - Possibly due to release of adsorbed water at higher temperatures.



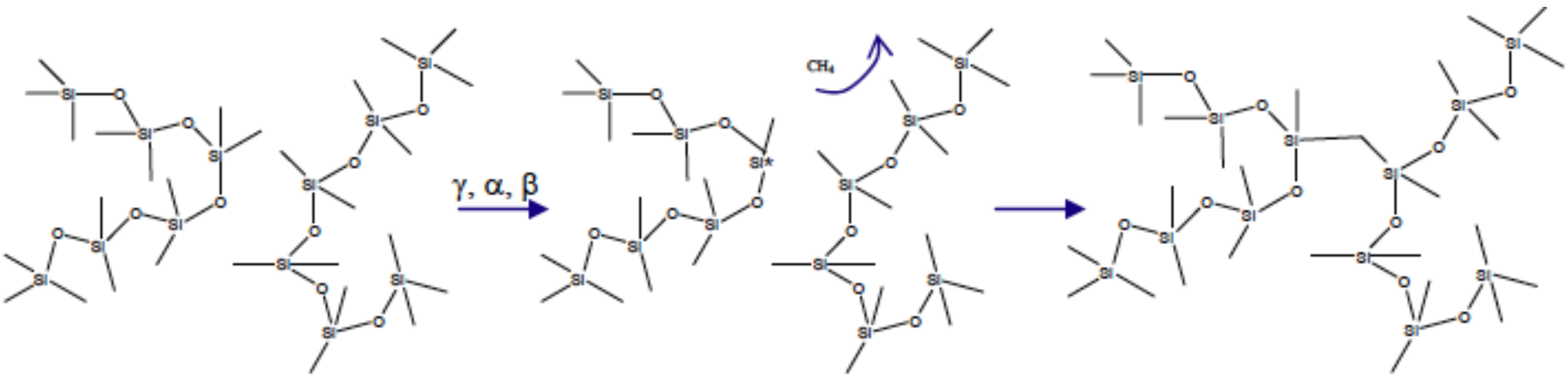
Historical Material Analysis- Radiolytic Aging (LLNL)

- **Spin-echo experiments using NMR-MOUSE and MRI.**
  - Increasing radiation dose= shorter T2
  - Material is getting stiffer,
  - Due to additional crosslinking.
- **In general, from swelling experiments, NMR, permanent set, and computed values the crosslink density of DC745U increases with radiation dose.**





Proposed Radiation Induced Crosslink Reaction



Radiation exposure induces a higher crosslink density in DC745U

Specific Knowledge Gaps that Remain

- **Further characterization of uncured DC745U, peroxide initiator, and filler.**
- **Develop relationship between mechanical testing of components and material samples.**
- **Investigate data used for current models and data needed to improve data prediction, e.g. lifetime prediction.**
- **Investigate how curing and post-curing conditions affects the material's overall properties and performance.**
- **Conduct additional low temperature mechanical tests with focus on soak time, temperature and thermal cycling.**

Objectives

- **Study how post-curing conditions affect the material's overall properties.**
  - DC745U has been marketed as not needing post-cure, however post-curing has always been used. Is post-curing needed or can the post-cure time be reduced?
  - Post-cure should increase crosslink density and reduce volatiles and residual peroxide initiator
  - Incomplete curing can lead to weak chemical linkages and physical interactions, and outgassing concerns.
  - Formulation, curing and post-curing conditions, heterogeneities, and production process can affect the long-term performance and compatibilty of the material.
- **Study low-temperature mechanical behavior of fully cured and post-cured material with the focus on soak time, load rate, and cycling.**
  - Investigate how low-temperature exposure of DC745U affects its mechanical properties and if the effect is reversible.

Characterization Techniques

- **Spectroscopic characterization**
  - Nuclear Magnetic Resonance: ^{1}H-NMR, Magic Angle Spinning Cross Polarization, Minispec ProFiler (spin-echo measurements)
  - Fourier Transform Infrared (FTIR)
- **Differential Scanning Calorimetry (DSC)**
- **Thermal Gravimetric Analysis coupled with FTIR and Mass Spectrometry (MS)**
- **Gas Chromatography coupled with Mass Spectrometry**
- **Dynamic Mechanical Analysis- DMA**
- **Mechanical Testing**

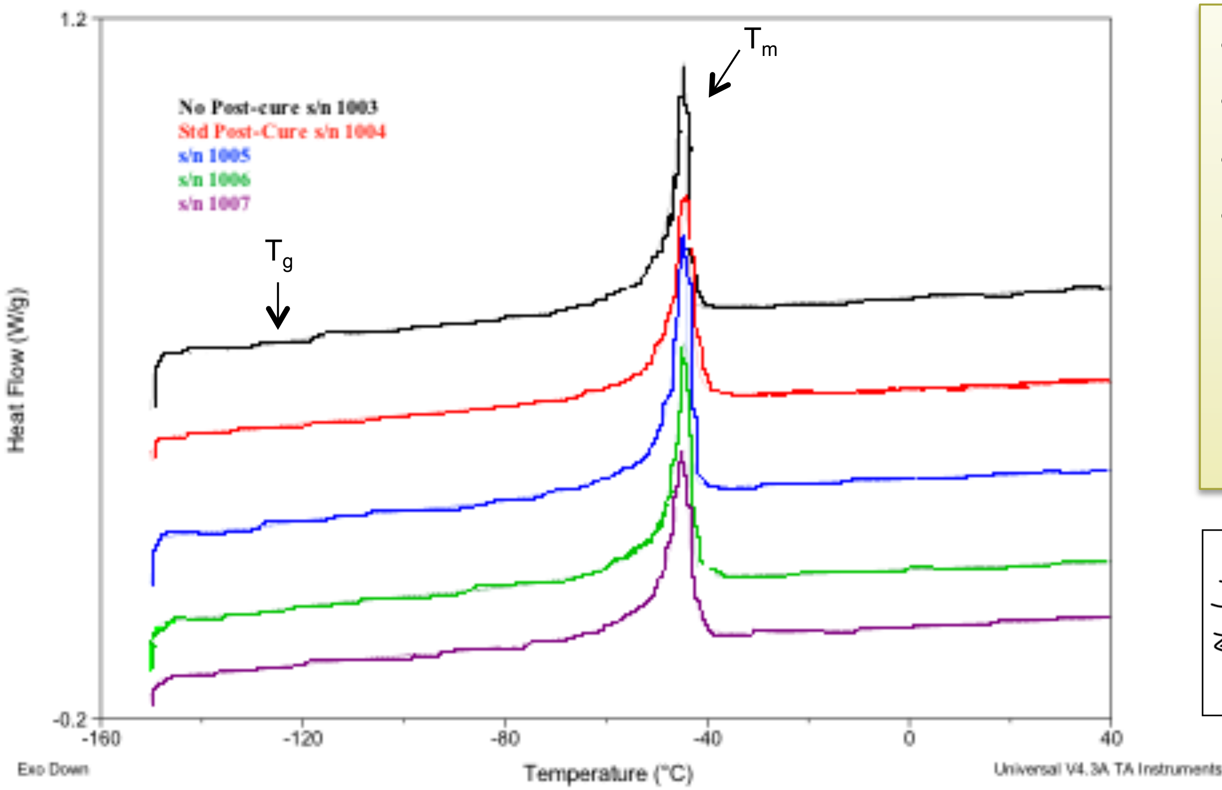
Post-cure Study: Samples

- Samples 1003-1007 were prepared from a full 6000g batch under the same molding conditions at the Kansas City Plant.
- Curing procedures varied as follows:

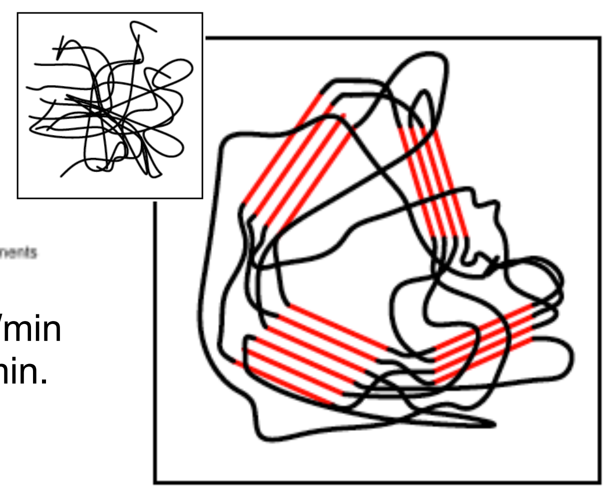
Sample	Curing	Post-curing	Post-curing
Raw Gum	-	-	-
1003	1 hr @ 160 ºC	-	-
1004	1 hr @ 160 ºC	1 hr @ 149 ºC	8 hrs @ 249 ºC
1005	1 hr @ 160 ºC	1 hr @ 149 ºC	4 hrs @ 249 ºC
1006	1 hr @ 160 ºC	1 hr @ 149 ºC	2 hrs @ 249 ºC
1007	1 hr @ 160 ºC	1 hr @ 149 ºC	-

* DC745U has been marketed as a material that does not need postcure.

Post-cure Study: DSC

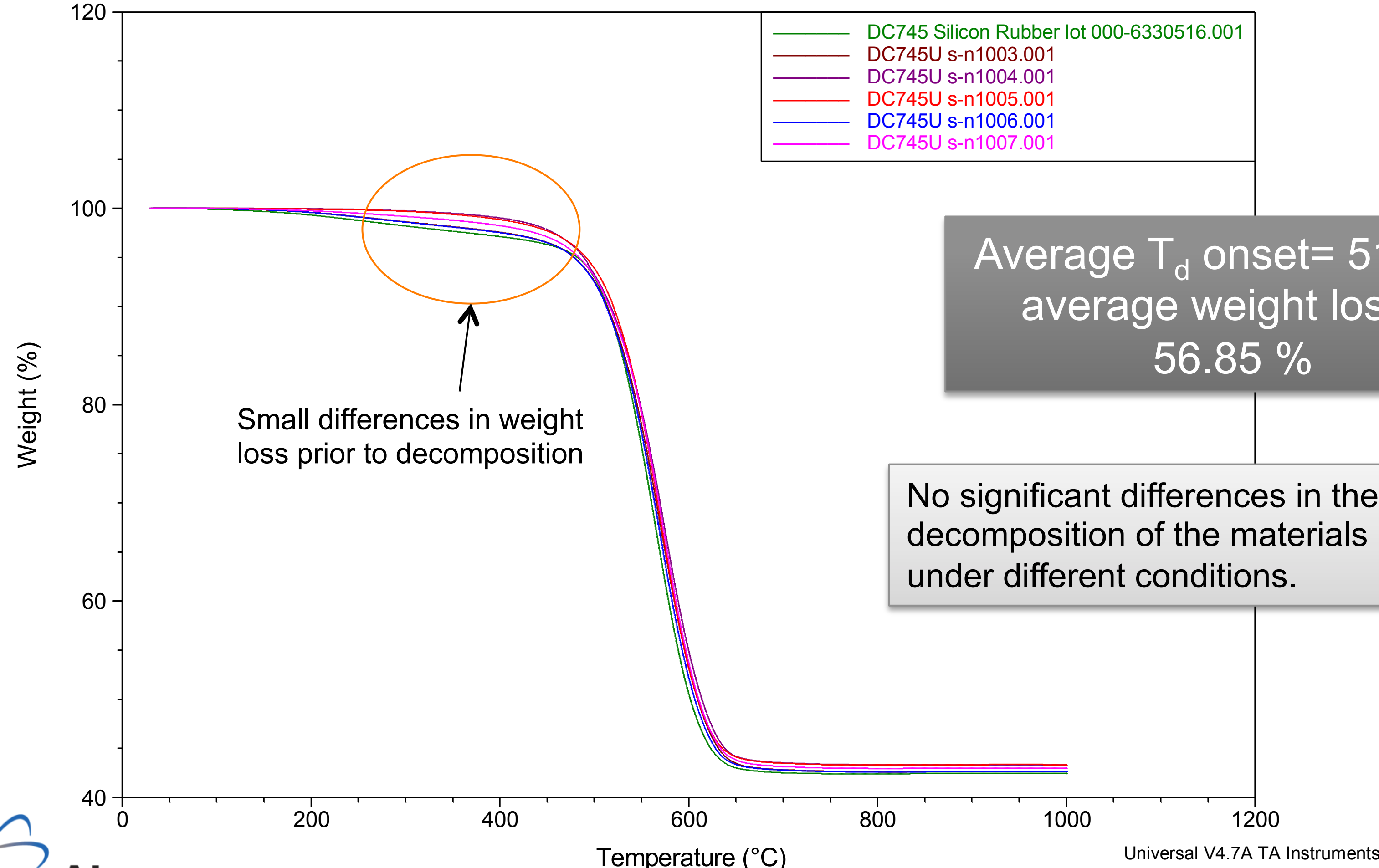


- T_g = -125 ºC
- T_m = ~ -45 ºC
- ΔH= ~16 J/g
- Variation on post-cure conditions has no significant effect on crystallinity.



Procedure: samples were rapidly cooled to -20ºC, then cooled at 2ºC/min to -150ºC. Samples were equilibrated at -150ºC then heated at 10ºC/min.

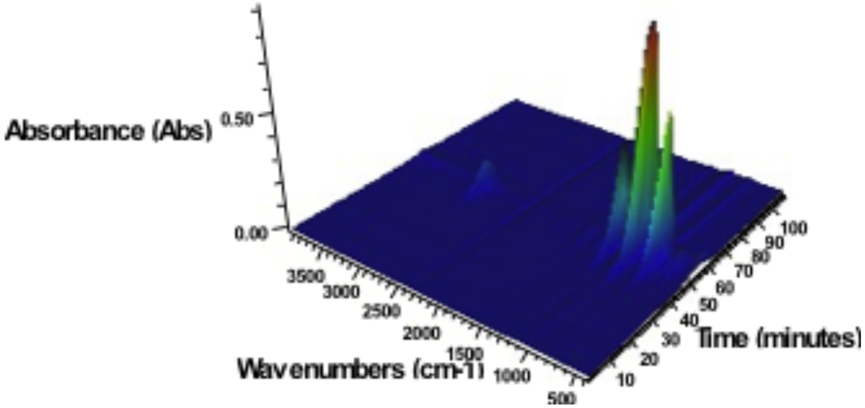
Post-cure Study: TGA

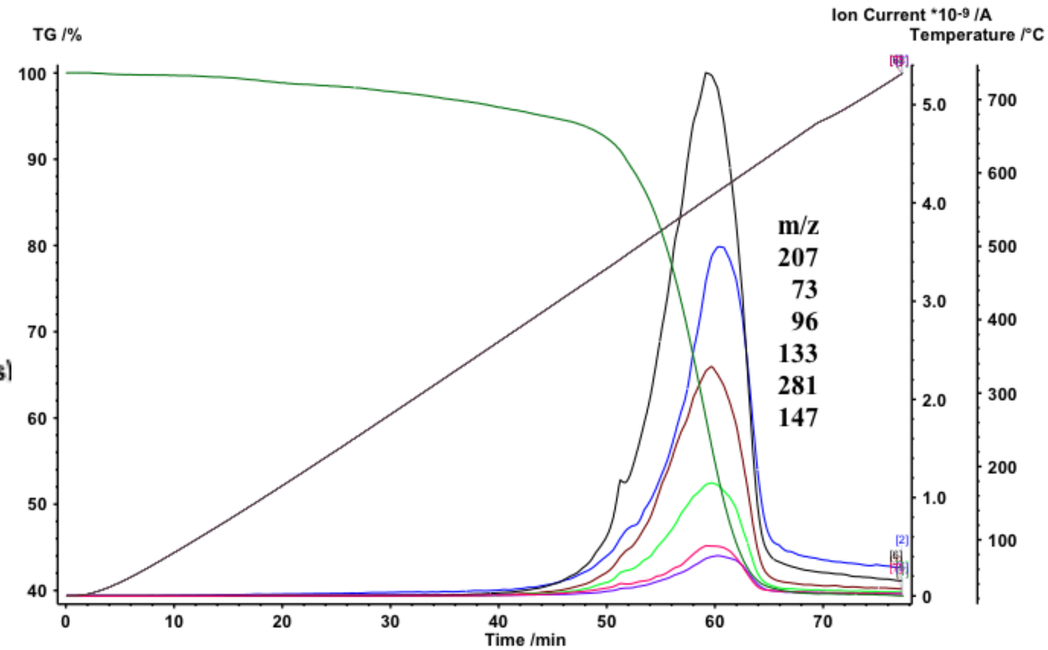


Average T_d onset= 513 ºC, average weight loss = 56.85 %

No significant differences in the onset of decomposition of the materials post-cured under different conditions.

Post-cure Study: FTIR and TGA/MS





Gas-phase FTIR shows:

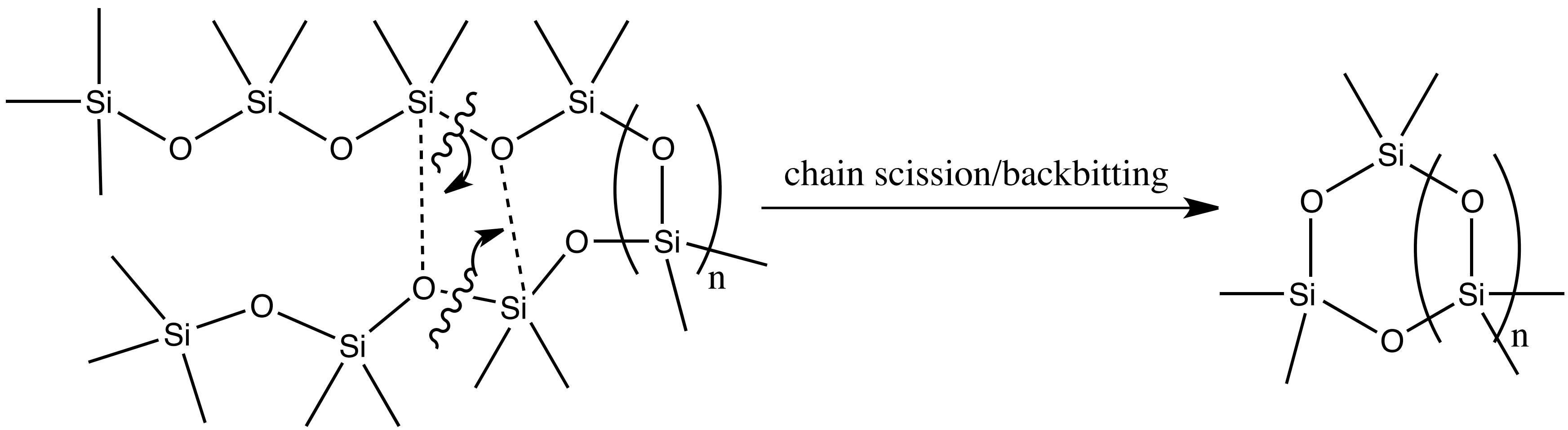
- The major decomposition products of DC745U are cyclic siloxanes.
- Siloxanes start to show on the FTIR at ~ 513 ºC.

Mass spectrometry shows:

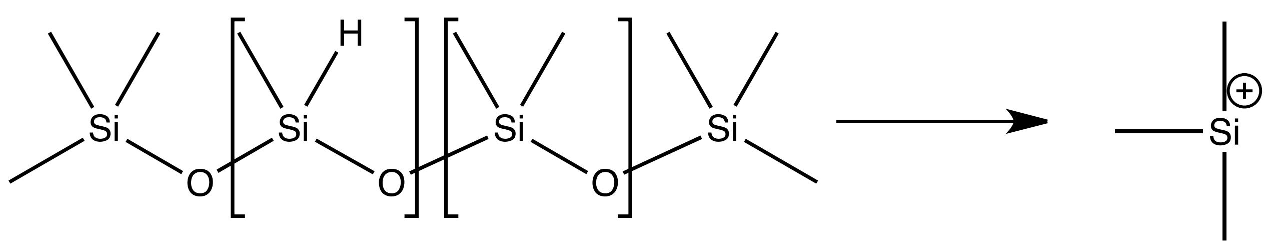
- The major decomposition product of DC745U is hexamethylcyclotrisiloxane (D_3, m/z 207).
- Other decomposition products are trimethylsilyl (m/z 73), octamethylcyclotetrasiloxane (D_4, m/z 281), and species that arise from D_3 and D_4 fragmentation.

Thermal Degradation Mechanism

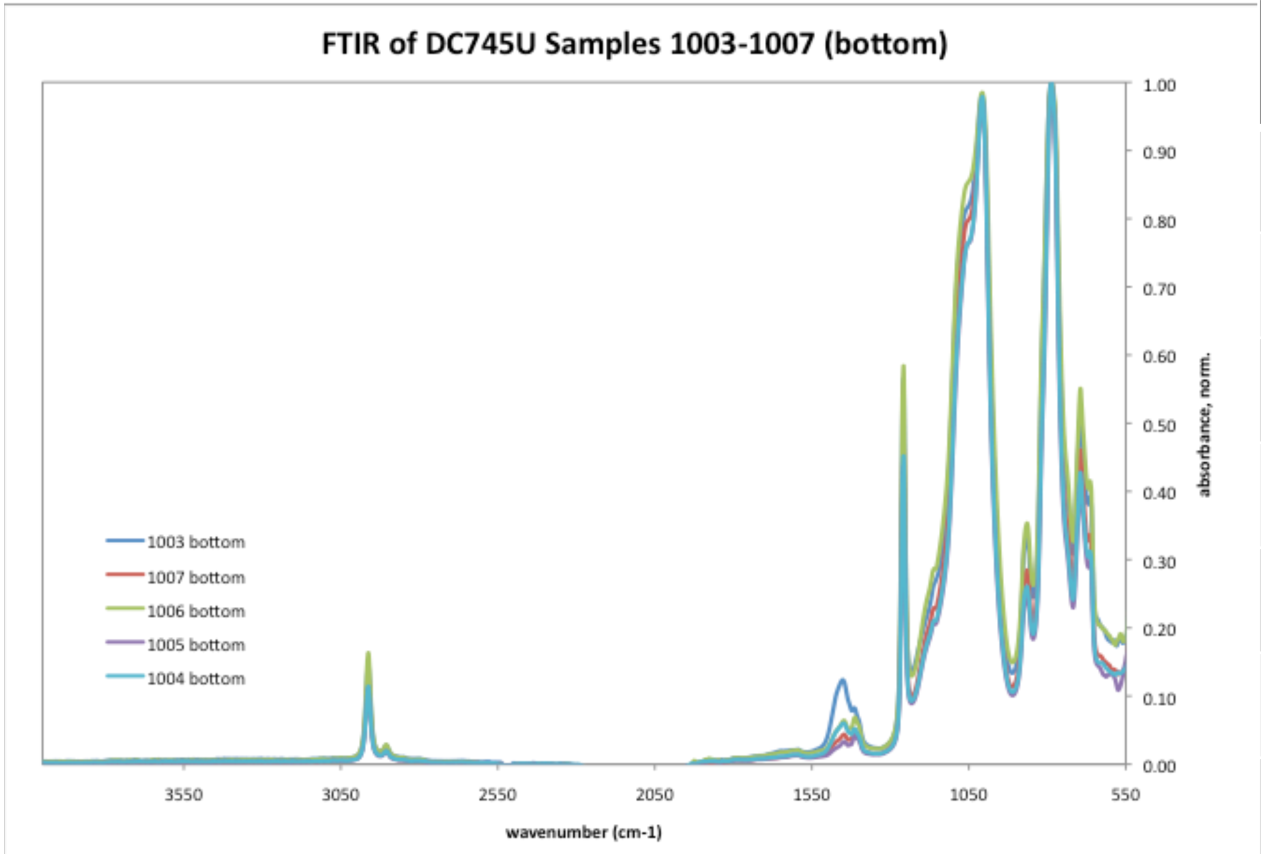
I. Formation of cyclic siloxanes



II. Formation of trimethylsilyl



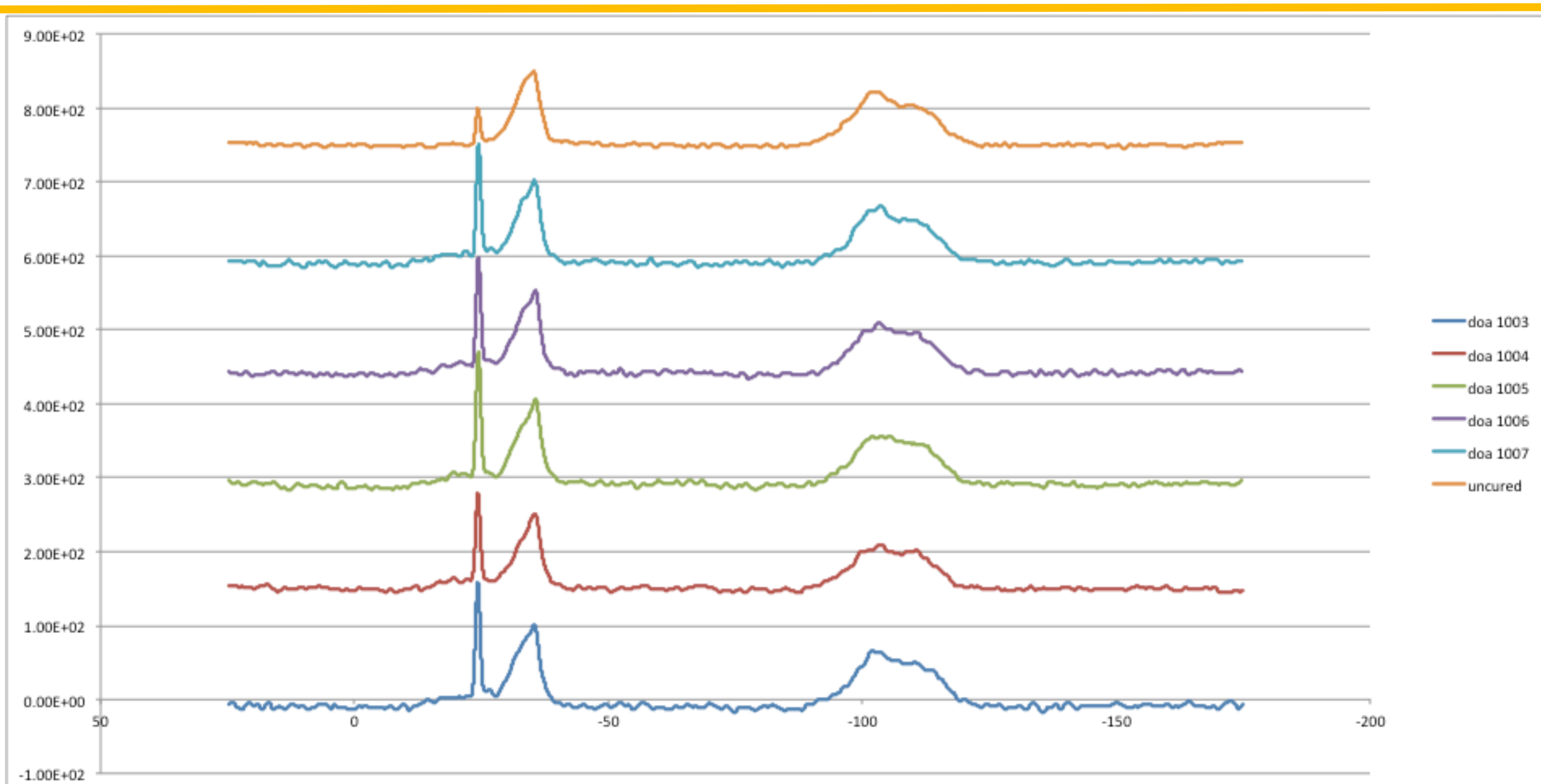
Post-cure Study: FTIR



Band (cm^{-1})	Assignment
866	Asymmetric strectching Si-OH
1008	Stretching Si-O-Si
1258	Symmetric deformation CH_3
1408	Asymmetric deformation CH_3
1448	C=C-H bend
2905	Symmetric stretching CH_3
2963	Asymmetric stretching CH_3

Spectra show larger amount of the C=C-H peak (at 1448 cm^{-1}) for the non post-cured sample 1003 likely because of incomplete curing reaction.

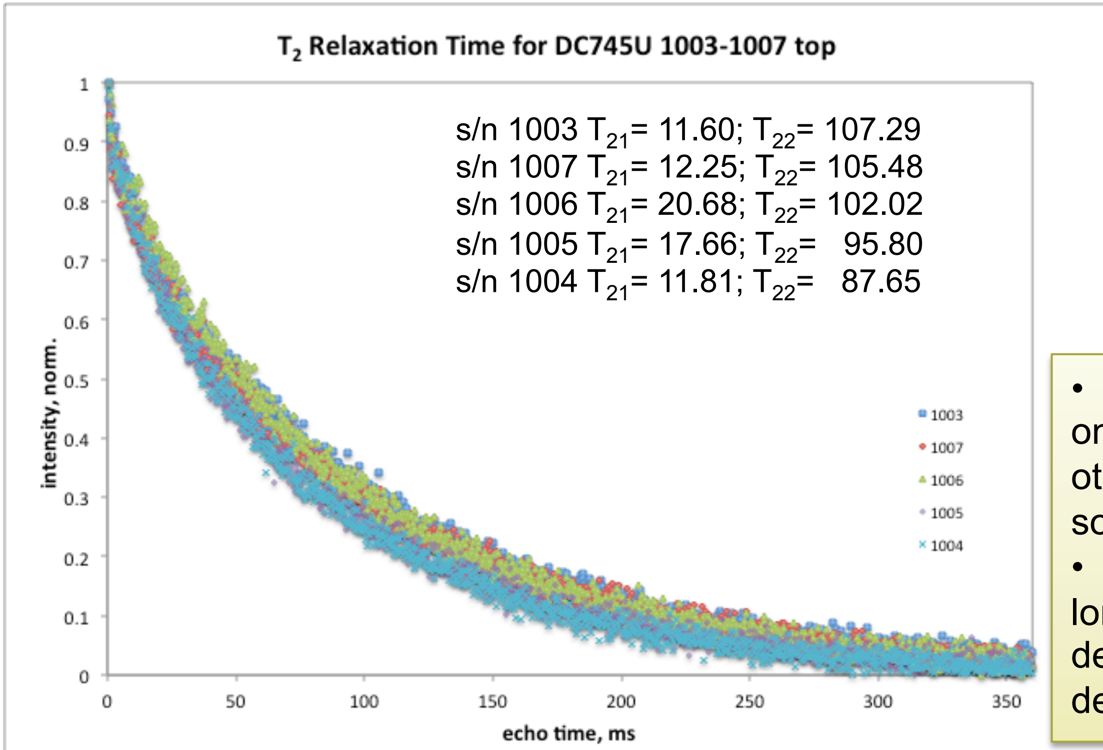
Post-cure Study: ^{29}Si CPMAS NMR



Four peaks are observed: -25 ppm (dimethyl), -34 ppm (methyl-phenyl), -101 ppm (silanol), and -109 ppm (siloxane). The peak at -25 ppm is smaller for the uncured samples because there is more mobility in the polymer resulting in less polarization during cross-polarization experiments.

Post-cure Study: Minispec ProFiler

- **Spin-echo experiments**



Method:
number of scans: 128
echoes: 1200
echo time: 0.30
pulse att.: 4dB
receiver gain: 103 dB
recycle delay: 1s

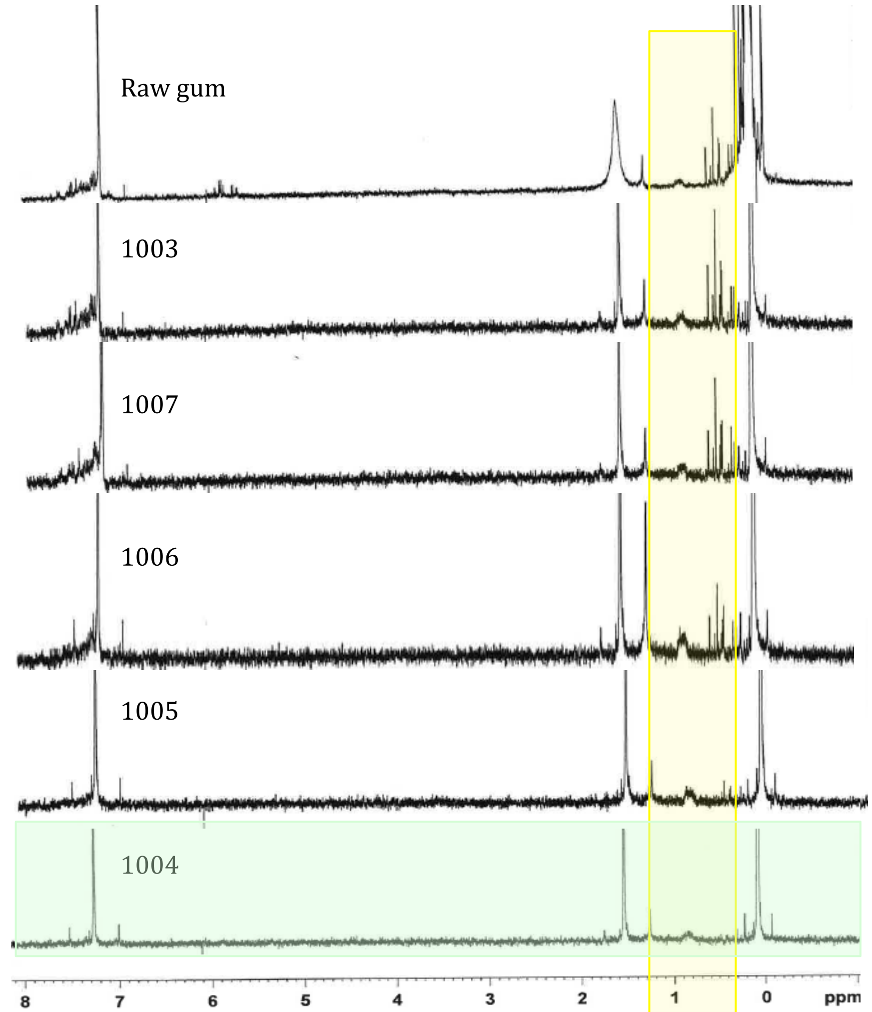
- Samples show two components of relaxation - one representing the polymer networks and the other representing the more mobile non-network sol fraction and dangling chain ends.
- Samples post-cured at high temperatures and longer time show a faster T_2 decay. Faster T_2 decay means lower mobility and higher crosslink density.

Post-cure Study: ^{1}H NMR of extracts

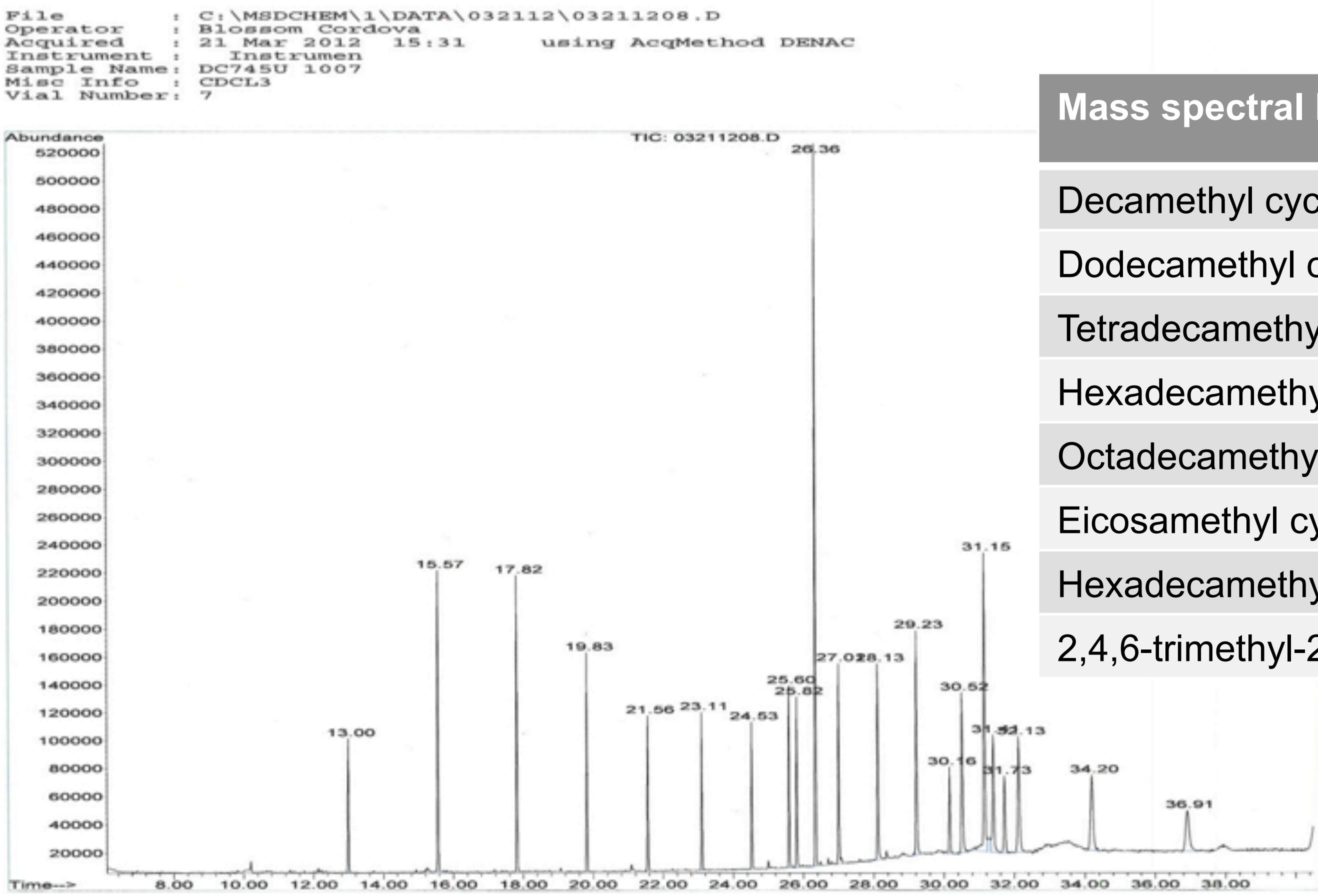
Solvent extraction: ~0.06 g of sample was stirred in 2 mL of $CDCl_3$ for 24 hours.

Samples cured for longer periods of time and at higher temperature show less amounts of extractable materials

Sample	Curing	Post-curing	Post-curing
Raw Gum	-	-	-
1003	1 hr @ 160 ºC	-	-
1004	1 hr @ 160 ºC	1 hr @ 149 ºC	8 hrs @ 249 ºC
1005	1 hr @ 160 ºC	1 hr @ 149 ºC	4 hrs @ 249 ºC
1006	1 hr @ 160 ºC	1 hr @ 149 ºC	2 hrs @ 249 ºC
1007	1 hr @ 160 ºC	1 hr @ 149 ºC	-



Post-cure Study: GC/MS of extracts



Mass spectral Results
Decamethyl cyclopentasiloxane
Dodecamethyl cyclohexasiloxane
Tetradecamethyl cycloheptasiloxane
Hexadecamethyl cyclooctasiloxane
Octadecamethyl cyclononasiloxane
Eicosamethyl cyclodecasiloxane
Hexadecamethyl cyclooctasiloxane
2,4,6-trimethyl-2,4,6-triphenyl cyclotrisiloxane

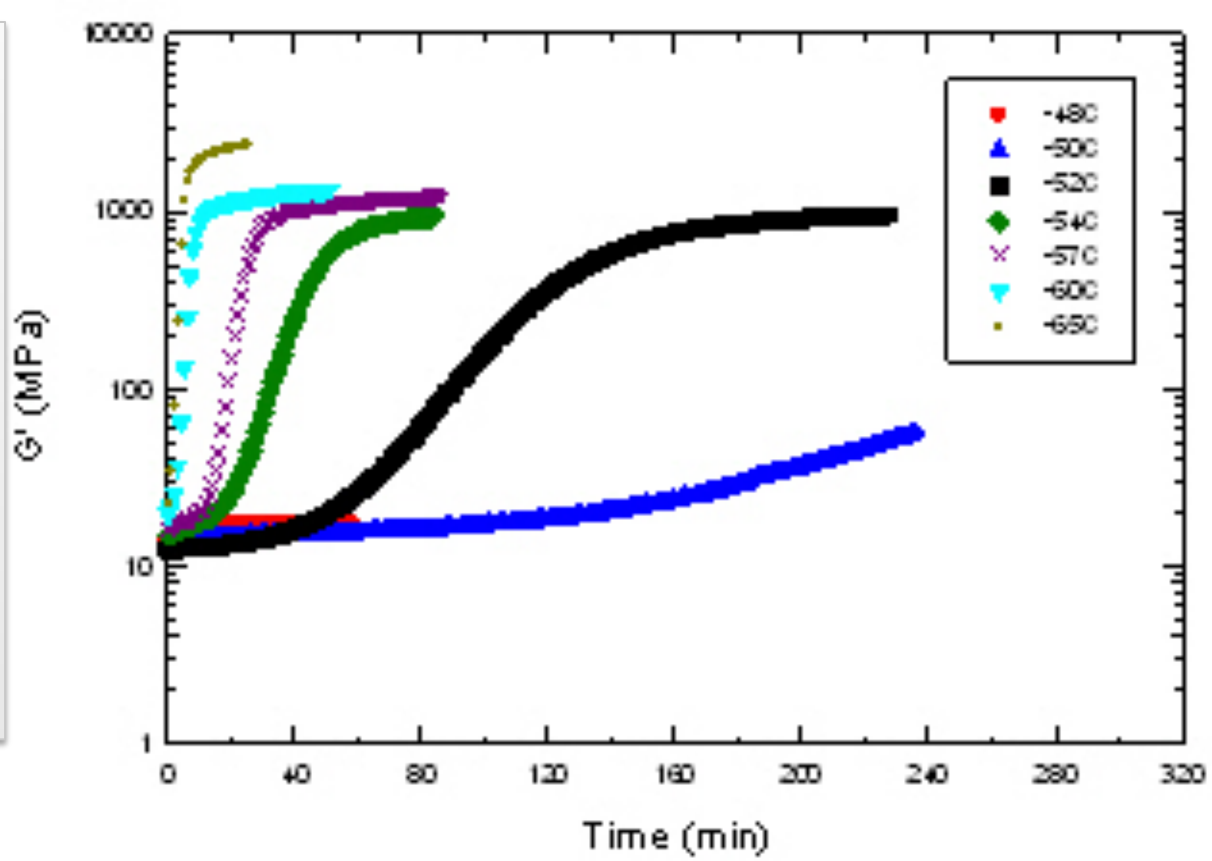
Post-cure Study: Summary and Conclusions

- TGA analyses show no significant differences in the decomposition behavior for samples cured and post-cure under several conditions.
- TGA/FTIR and TGA/MS suggest that DC745U degrades mainly by a chain-scissioning/ backbitting mechanism with the main degradation product been cyclic siloxanes.
- DSC show no significant differences on crystallinity for samples cured and post-cured under various conditions.
- Curing conditions shown here do have an impact in the materials properties based in the amount of low MW compounds (extractables) left after curing and the crosslink density determined by spin echo NMR experiments.
- NMR and GC/MS performed on extracts show the presence of cyclic siloxanes with lower quantities for materials cured for longer period of time.
- *Even though DC745U has been marketed as a material that does not require postcure, we have found that postcure reduces the presence of low MW volatiles and increases the detectable cross link density (NMR). Postcuring peroxide-cured siloxanes also reduces residual peroxide species. All of these factors, can impact the long term mechanical properties (compression set) and outgassing.*

Low Temperature Mechanical Behavior: DMA

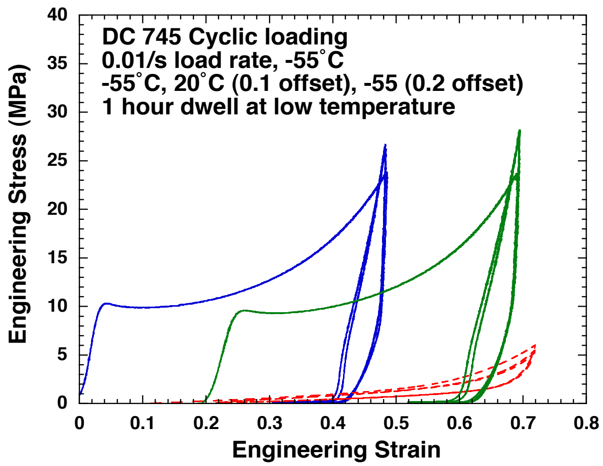
To understand the effect crystallinity has on the mechanical properties of DC745U:

- Crystallization has a significant effect on mechanical properties.
- Crystallization causes the G’ to increase by two-orders of magnitude.
- Crystallization is not an instantaneous process.



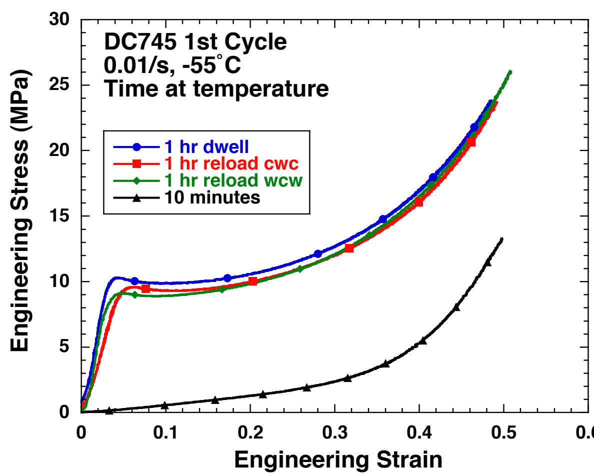
Procedure: Isothermal measurements.

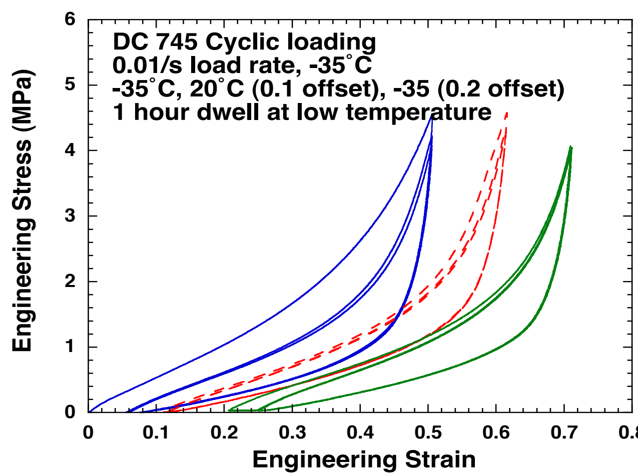
Low Temperature Mechanical Behavior



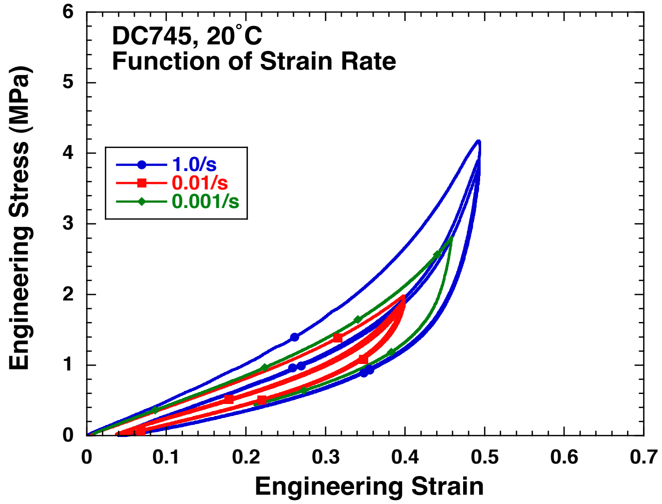
Crystalline Transition:

- There is a transition at ~ -55°C.
- The transition is a kinetically driven process- takes ~ 1 hour at temperature to happen.
- No transition observed at warmer temperatures - behavior is visco-elastic.



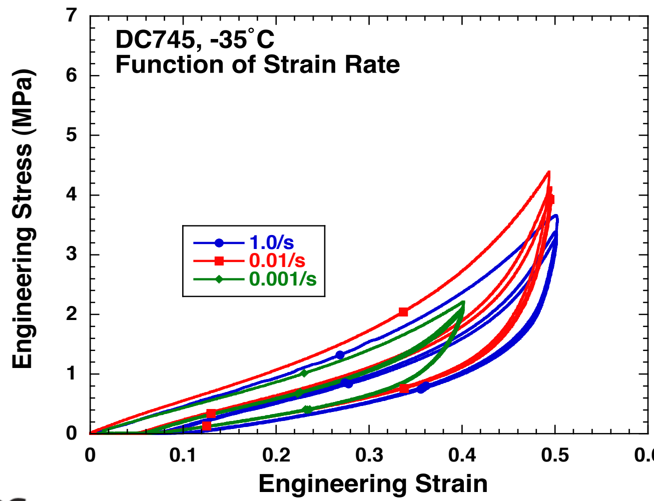


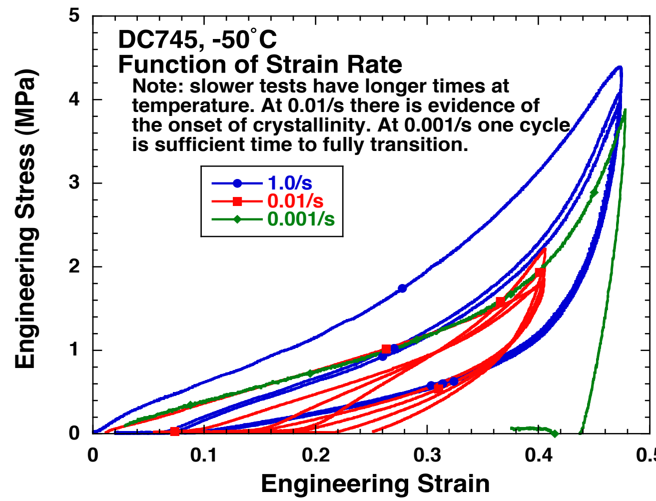
Low Temperature Mechanical Behavior



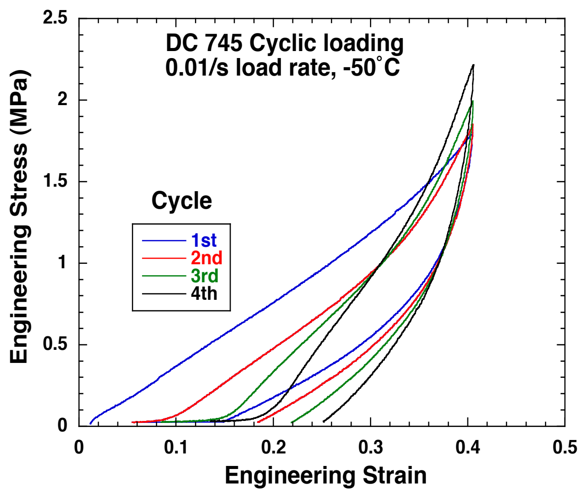
Strain Rate and Temperature Effect:

- At warm temperatures (20 and -35 ºC) no transition is observed regardless of strain rate.
- At cold temperature (-50 ºC) rate does have an effect. Transition is observed at slower rate (0.001/s).



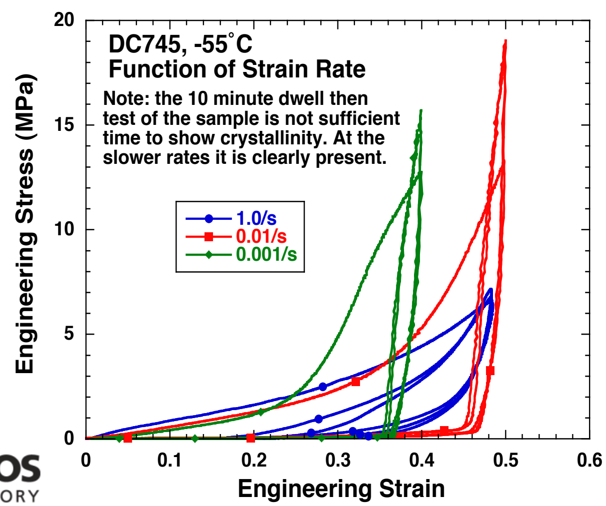


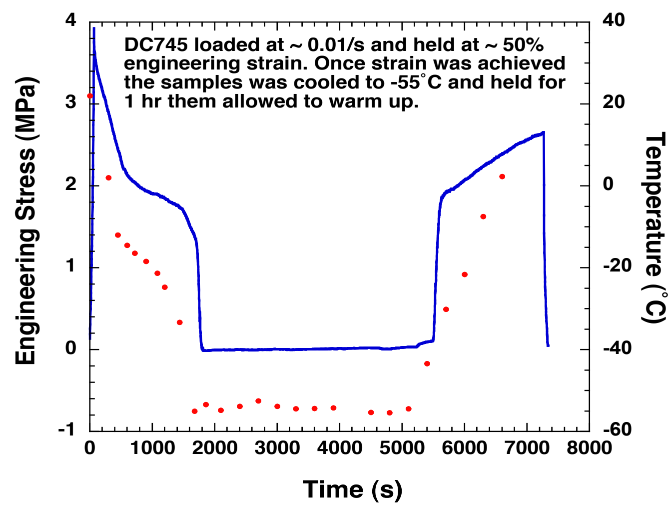
Low Temperature Mechanical Behavior



Time at temperature and cooling under load

- Crystalline transition is clearly present at a lower temperature (-55 ºC) and slower rate (0.01/s and 0.001/s).
- Time at temperature does have an impact of crystalline transition.
- Material held at constant compressive displacement and cooled.
  - As the sample cools the load drops, drops very rapidly near "transition".
  - Material recovers rapidly at temperatures above -40 ºC.





Summary and Conclusion

- DMA shows that crystallization does have an effect on the mechanical properties of DC745U.
- DMA shows that the crystallization is time and temperature dependent.
- Mechanical tests show that DC745U undergo a crystalline transition at temperatures below -50 ºC.
- Rate and temperature does not have an effect above crystalline transition.
- Crystalline transition occurs faster at colder temperatures.
- The material remains responsive and recovers after warming it to temperature above -40 ºC.

Overall Conclusions

- We were able to review all previous historical data on DC745U.
- Identified specific gaps in materials understanding.
- Developed design of experiments and testing methods to address gaps associated with post-curing and low temperature mechanical behavior.
- Resolved questions of post-cure and alleviated concerns associated with low temperature mechanical behavior with soak time and temperature.
- This work is relevant to mission-critical programs and for supporting programmatic work for weapon research.

Acknowledgment

- This work was supported by LANL Enhanced Surveillance Campaign-Campaign 8
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- Bruce Orler (formerly MST-7)