Title: New Experimental Data in DC745U

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Intended for: Campaign 2 meeting

New Experimental Data in DC745U

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C-CDE: Chemical and Diagnostic Engineering Group and
MST-8: Materials Science in Radiation and Dynamic Extremes

June 20th, 2012

Campaign 2 Meeting

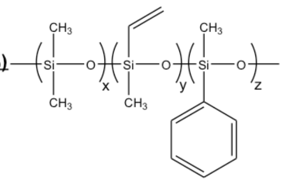
Objectives

- **Study the molecular and mechanical properties of DC745U.**
  - DC745U is a silicone elastomer used in several weapon systems.
  - Depending on their chemistry and formulation, polymers can be susceptible to damage and failures due to weak chemical linkages and physical interactions.
  - Inefficient production processes can generate heterogeneitites throughout the material that can contribute negatively to the overall performance and lifetime of the polymer.
  - Aging, long-term thermal and radioactive conditions, and mechanical strains can affect the material's network structure and contribute to the degradation of the product.
- **Characterization of DC745U materials cured under different conditions to determine possible differences to the polymer structure.**
- **This work is relevant to mission-critical programs and for supporting programmatic work for weapon research.**

DC745U- Composition

- ^{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.

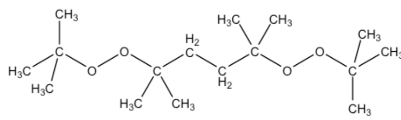
Polysiloxane (99.5%)



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

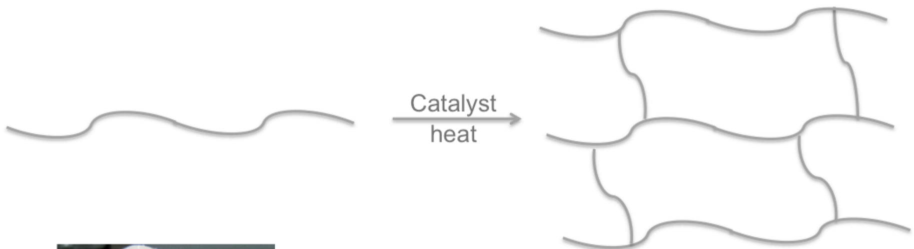
Manufactured by Dow Corning, initially under the name of Silastic® DC745U. Currently available through Xiameter® or R.D. Abbott Company

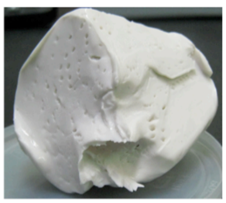
Peroxide Curing Agent (0.5%)



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





Curing conditions will determine the crosslink density, and thus the properties of the final product.

Characterization Techniques

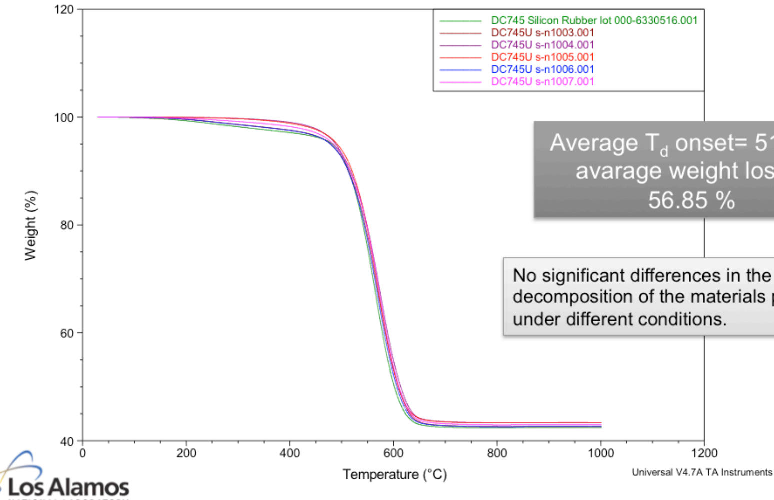
- **Spectroscopic characterization**
  - Nuclear Magnetic Resonance: ^{1}H-NMR, Magic Angle Spinning Cross Polarization, Minispec ProFiler (spin-echo measurements)
  - Fourier Transform Infrared (FTIR)
- **Thermal Gravimetric Analysis coupled with FTIR and Mass Spectrometry (MS)**
- **Gas Chromatography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

DC745U Samples Analyzed in these studies

- Samples 1003-1007 were prepared from a full 6000g batch under the same molding conditions in 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 ºF	8 hrs @ 249 ºF
1005	1 hr @ 160 ºC	1 hr @ 149 ºF	4 hrs @ 249 ºF
1006	1 hr @ 160 ºC	1 hr @ 149 ºF	2 hrs @ 249 ºF
1007	1 hr @ 160 ºC	1 hr @ 149 ºF	-

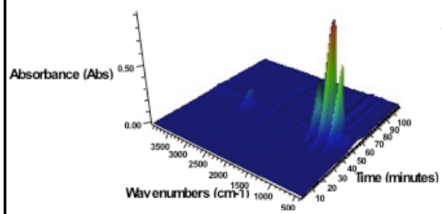
TGA Profiles for DC745U Samples

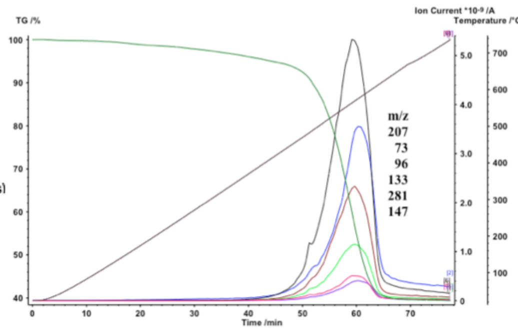


Average T_d onset= 513 °C, avarage weight loss = 56.85 %

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

FTIR and TGA/MS





Gas-phase FTIR shows:

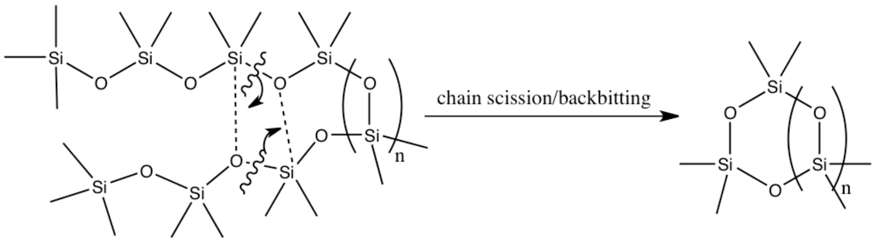
- The major decomposition products of DC745U are cyclic siloxanes.
- Siloxanes start to show on the FTIR at ~ 513 ºC.

Mass spectrometry shows:

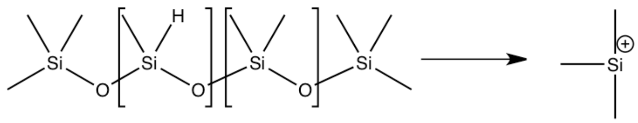
- The major decomposition product of DC745U is hexamethylcyclotrisiloxane (D_3, m/z 207).
- Other decomposition products are trimethylsilyl (m/z 73), octamethylcyclotetrasiloxane (D_4, m/z 281), and species that arise from D_3 and D_4 fragmentation.

Thermal Degradation Mechanism of DC745U

I. Formation of cyclic siloxanes



II. Formation of trimethylsilyl



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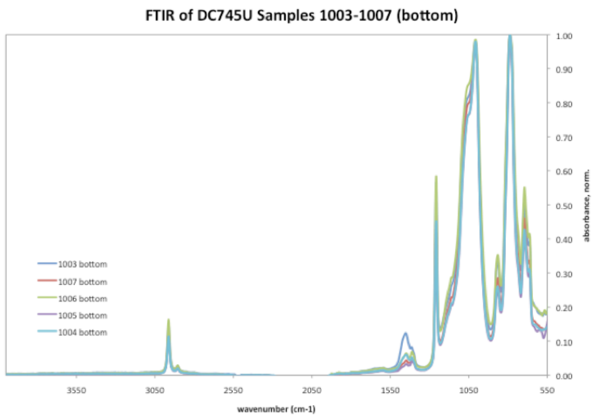
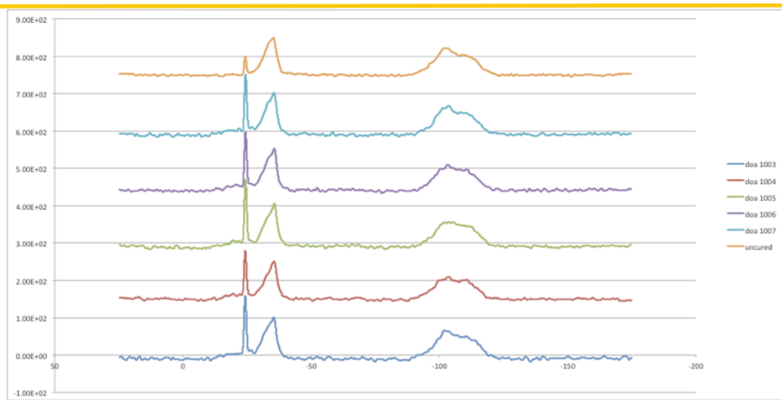
FTIR Spectra for DC745U Samples



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

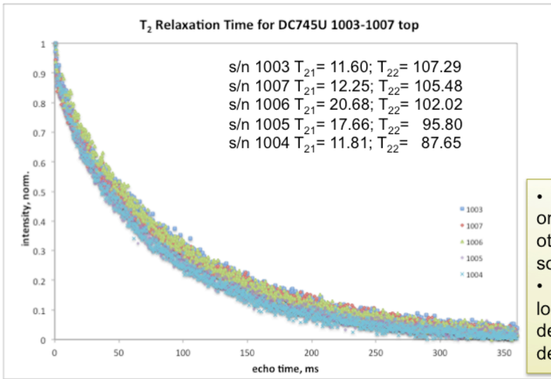
Spectra show larger amount of the C=C-H peak (at 1448 cm^{-1}) for the non post-cured sample 1003 likely because of incomplete curing reaction.

^{29}Si CPMAS NMR for DC745U Samples



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.

Spin-echo NMR Experiments using Minispec ProFiler



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.

^1H NMR Spectra for extracted materials from DC745U samples

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 ºF	8 hrs @ 249 ºF
1005	1 hr @ 160 ºC	1 hr @ 149 ºF	4 hrs @ 249 ºF
1006	1 hr @ 160 ºC	1 hr @ 149 ºF	2 hrs @ 249 ºF
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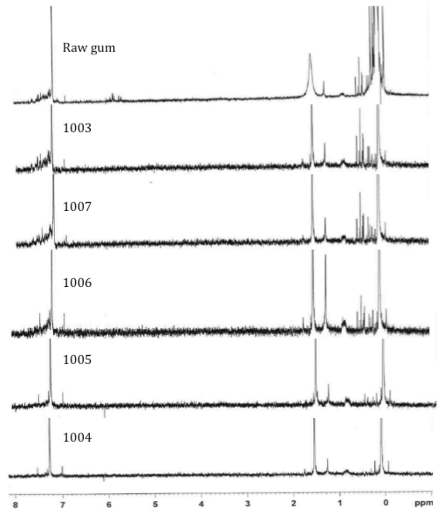
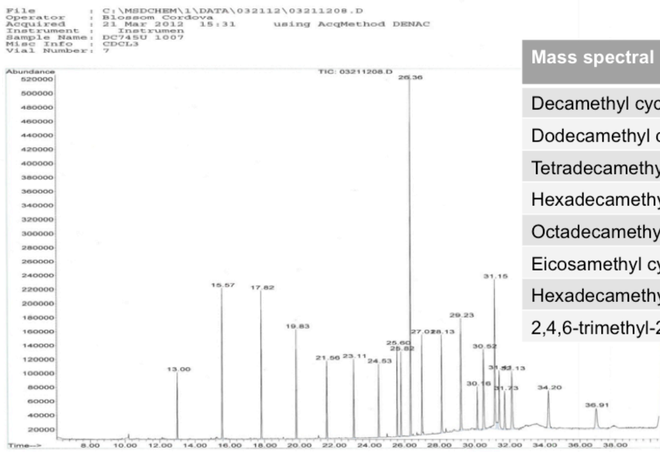
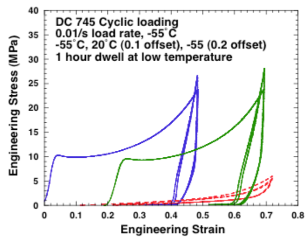


GC/MS Data for extracted materials from DC745U samples



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

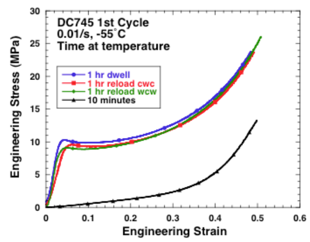
Mechanical Characterization as a Function of Strain Rate and Temperature – Crystaline Transition

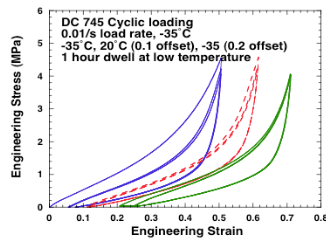


Crystaline Transition:

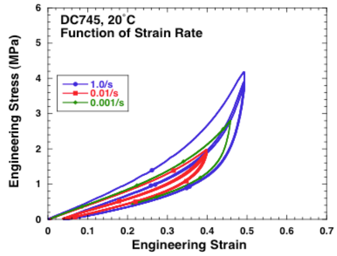
- There is a transition at ~ -50°C.
- The transition is a kinetically driven process.
- At warmer temperatures the behavior is visco-elastic

Note: upper left and lower right shows data taken for 1 hr dwell at temperature before testing. Data has been offset for clarity. No transition in warmer tests. Room temp loading between cold tests to see in permanent damage created.





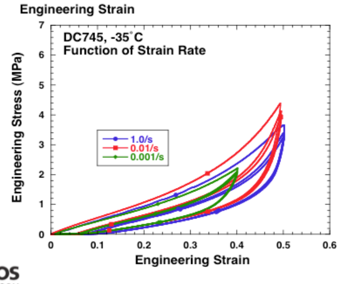
Mechanical Characterization as a Function of Strain Rate and Temperature

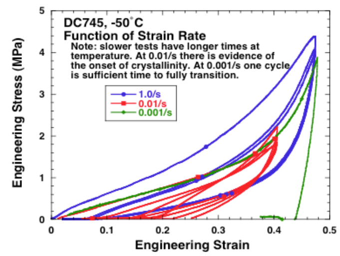


Strain Rate and Temperature Effect:

- There is little effect of strain rate above the crystaline transition.
- Appears to have little temperature sensitivity as well.

Note: 10 minute dwell at temp before testing. In the lower right plot the data are holding shape as more of the material “transitions”. At -50°C the transition is relatively slow. At high rates the test is over quickly and little material transitions.





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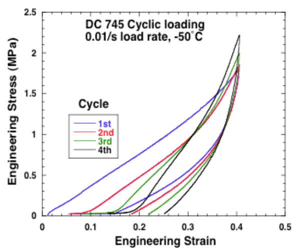
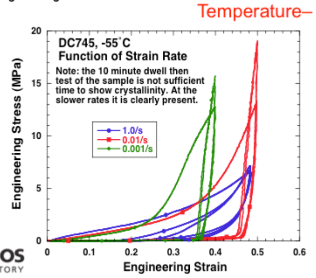
Mechanical Characterization – Time at Temperature and cooling under load

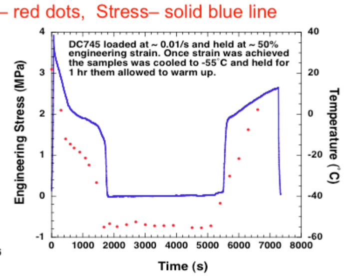


- The plots on left illustrate the kinetic response in the “transition”
- Material held at constant compressive displacement and cooled.
- As the sample cools the load drops, drops very rapidly near “transition”,
- recovers rapidly above “transition”.

Note: 10 minute dwell at temp before testing. Gradual transition at -50°C, much more rapid at -55°C. Notice that even at -55°C that the transition takes less time than it takes to finish the test at high rate.

Temperature– red dots, Stress– solid blue line





Summary and Conclusion

- **TGA analyses show no significant differences in the decomposition behavior for samples cured 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.**
- **Curing conditions shown here do have an impact in the materials properties based in the amount of low MW compounds 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.***

Acknowledgment

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- Blossom Cordova