LA-UR-12-23612
Approved for public release; distribution is unlimited.

Title:	Historical Material Analysis of DC745U Pressure Pads
Author(s):	Ortiz-Acosta, Denisse
Intended for:	Report

Historical Material Analysis of DC745U Pressure Pads

Denisse Ortiz-Acosta and Crystal G. Densmore
Los Alamos National Laboratory

Mission Statement
As part of the Enhance Surveillance mission, it is the goal to provide suitable lifetime assessment of stockpile materials. This report is an accumulation of historical publication on the DC745U material and their findings. It is the intention that the B61 LEP program uses this collection of data to further develop their understanding and potential areas of study.

Acknowledgments
Tom Zocco C8 Program Manager
Steve Birdsell C8 Polymers Work Package SME

TABLE OF CONTENTS

EXECUTIVE SUMMARY

DC745U is a commercially available silicone elastomer consisting of dimethyl, methyl-phenyl, and methyl-vinyl siloxane repeat units. Originally, this material was manufactured by Dow Corning as Silastic® DC745U at their manufacturing facility in Kendallville, IN. Recently, Dow Corning shifted this material to the Xiameter® brand product line. Currently, DC745U is available through Xiameter® or Dow Corning's distributor R. D. Abbott Company.

DC745U is cured using 0.5 wt% vinyl-specific peroxide curing agent known as Luperox 101 or Varox DBPH-50. This silicone elastomer is used in numerous parts, including two major components (outer pressure pads and aft cap support) in the W80 and as pressure pads on the B61. DC745U is a proprietary formulation, thus Dow Corning provides limited information on its composition and properties. Based on past experience with Dow Corning, DC745U is at risk of formulation changes without notification to the costumer. A formulation change for DC745U may have a significant impact because the network structure is a key variable in determining material properties.

The purpose of this report is to provide an overview of historical DC745U studies and identify gaps that need to be addressed in future work. Some of the previous studies include the following:

1. Spectroscopic characterization of raw gum stock.
2. Spectroscopic, thermal, and mechanical studies on cured DC745U.
3. Nuclear Magnetic Resonance (NMR) and solvent swelling studies on DC745U with different crosslink densities.
4. NMR, solvent swelling, thermal, and mechanical studies on thermally aged DC745U.
5. NMR, solvent swelling, thermal, and mechanical studies on radiolytically aged DC745U.

Each area is reviewed and further work is suggested to improve our understanding of DC745U for systems engineering, surveillance, aging assessments, and lifetime assessment.

1.0 COMPOSITIONAL ANALYSIS

1.1 Lawrence Livermore National Laboratory[1]

The methods used for the structural analysis of DC745U uncured materials included solution state ^{1}H-NMR, ^{29}Si-Magic Angle Spinning (MAS)-NMR, Multi Quantum (MQ)-NMR, and Fourier Transform Infrared (FTIR) spectroscopy. ^{29}Si MAS-NMR shows that DC745U contains small amounts of methyl-phenyl siloxane with a peak at -38 ppm, and approximately 30% wt of SiO_2 used as filler with peaks at -100 ppm and -110 ppm, as shown in Figure 1A. From the solution-state ^{1}H NMR shown in Figure 1B it was determined that the material has a monomer ratio of approximately 100:1.5 dimethyl to methylphenyl siloxane.

MQ-NMR suggests that the network structure of DC745U is complex with at least a bimodal network structure of high and low crosslink density. The high crosslink density area was assigned to polymer chains that are interacting with the filler. NMR experimental details are described in Appendix I and II.

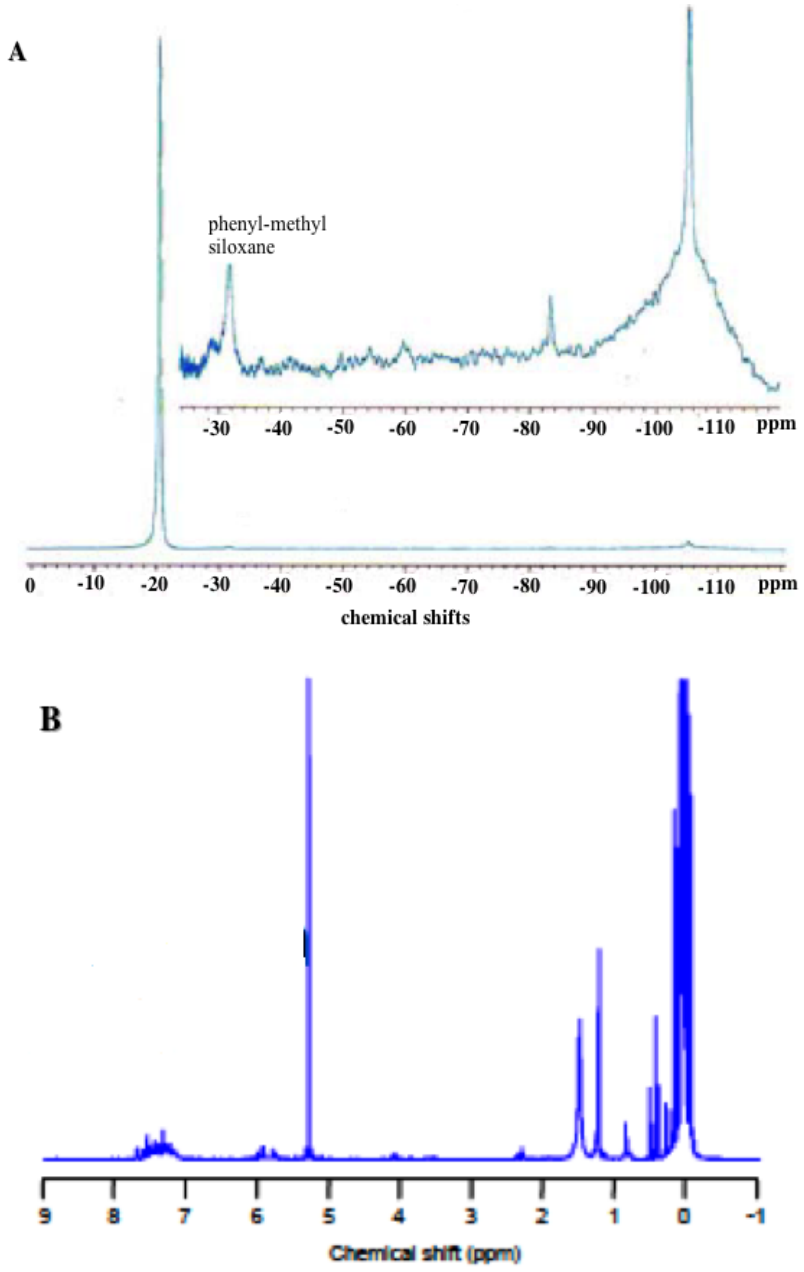


Figure 1. (A) ^{29}Si- MAS NMR and (B) solution state ^{1}H-NMR (from CD_2Cl_2) of uncured DC745U.

FTIR of uncured DC745U confirms the dominant presence of dimethyl siloxane units, phenyl groups present in small quantities, and the presence of condensed silicates that are used as filler. The FTIR spectra are shown in Figure 2.

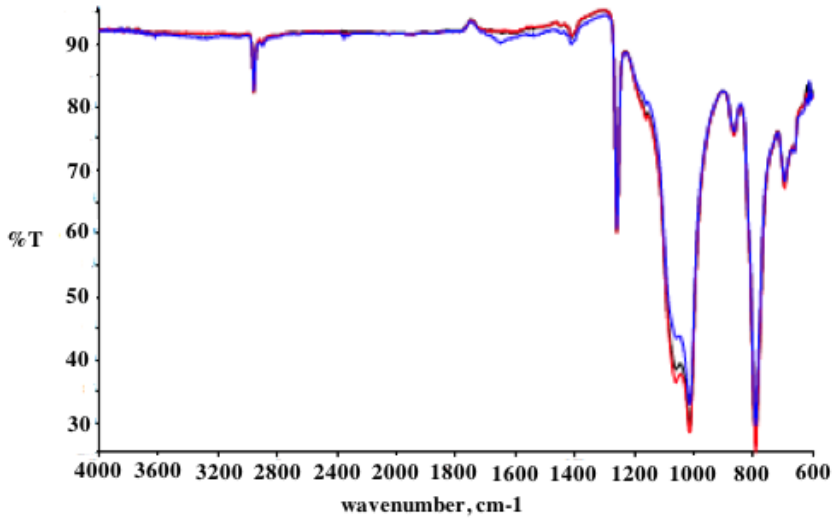


Figure 2. FTIR spectra of three representative DC745U samples.

1.2 Washington and Jefferson College and Los Alamos National Laboratory[2]

The NMR analyses for the uncured DC745U materials involved cross-polarization (CP) ^{29}Si-NMR and single pulse direct polarization ^{1}H-NMR. The ^{1}H-NMR spectrum (Figure 3A) revealed a high intensity signal at 0 ppm that corresponds to dimethylsiloxane groups. Peaks between 1 ppm and 8 ppm are assigned to silanol protons in fumed silica with varying degree of hydrogen bonding. Peaks between 3 ppm and 5 ppm are due to water protons adsorbed to the silica surface. Peaks at 2 ppm, 3.5 ppm, 4.1 ppm, and 4.9 ppm are designated to isolated silanol protons, water physisorbed to the silica, water exchange between the liquid and physisorbed environments, and water in humidified silica, respectively. A peak at 5 pm corresponds to the center of hydrogen bonding of silanols.

The ^{29}Si-NMR spectrum, shown in Figure 3B, shows a high intensity peak at -20.5 ppm that corresponds to the dimethylsiloxane groups. In addition, the blown up ^{29}Si-NMR spectrum of the uncured material shows peaks at -32 ppm that corresponds to phenyl groups. Peaks between -80 ppm and -115 ppm are assigned to inorganic fumed silicates. The peaks at -80 ppm, -99 ppm, and -109 ppm correspond to geminal silanol, single silanol, and siloxane, respectively. The peak at -110 ppm is designated to crystalline quartz.

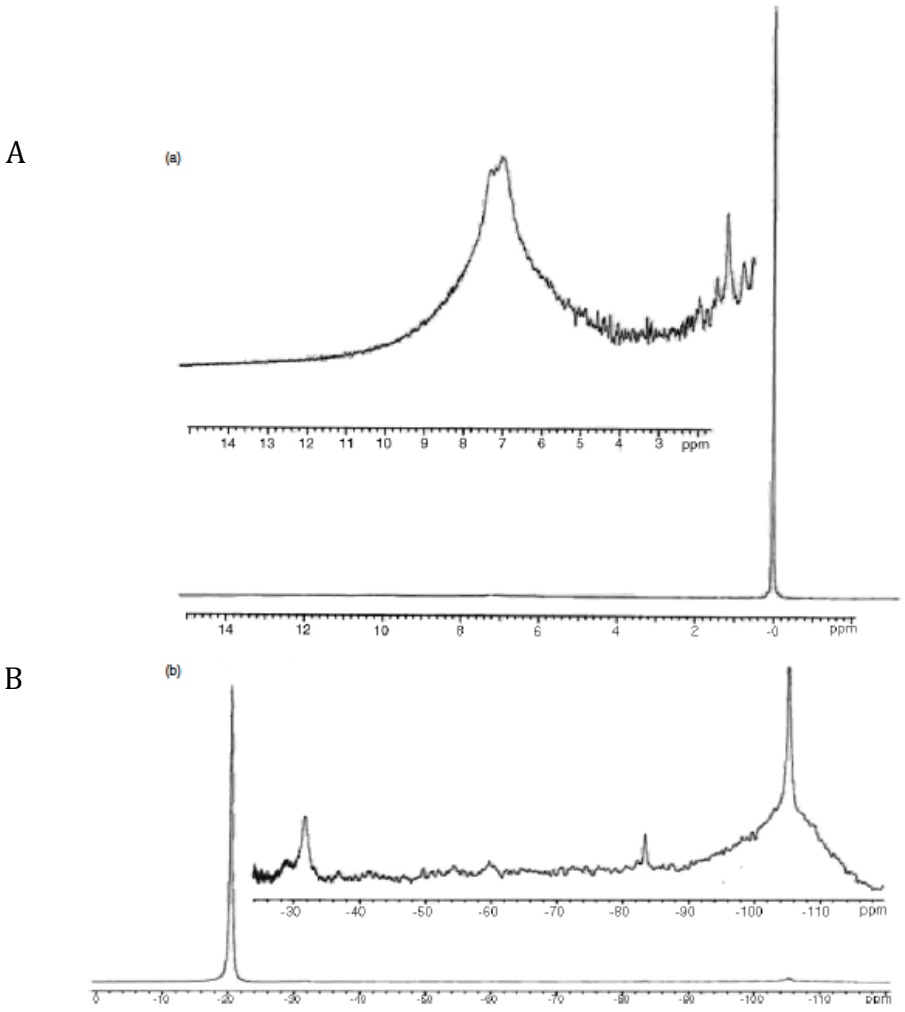


Figure 3. Single-pulse excitation ^{1}H- (A) and ^{29}Si- (B) NMR spectra of uncured DC745U.

^{1}H/^{29}Si cross-polarization NMR experiments were performed to study the interface between PDMS and the filler. Cross-polarization (cp) experiments are often used to improve signal-to-noise by making a heteronuclear transfer of magnetization from an abundant to a dilute spin system; however, the results are not quantitative. In the case of DC745U, cp edits or filters the ^{29}Si spectrum by decreasing the signal that corresponds to the mobile phase or eliminating peaks that are not in spatial proximity to hydroge. The cp spectrum of the uncured DC745U material shows enhanced peaks that correspond to the smaller amounts of inorganic and substituted polymer components. The spectrum, shown in Figure 4, shows the presence of the phenyl peak at -33 ppm. In addition, it shows the peaks of the two inorganic silicates at -99 ppm and -109 ppm that corresponds to single silanol and siloxane, respectively. A shoulder at approximately -85 ppm

is also observed. The cp spectrum of the uncured DC745U does not show a sharp peak at -110 ppm (assigned to quartz).

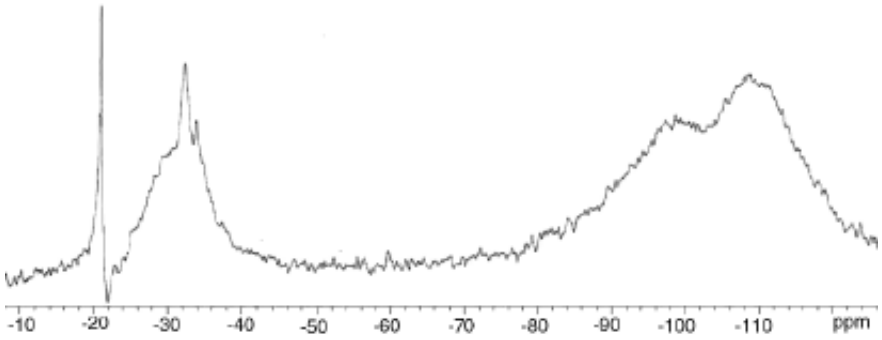


Figure 4. The cp/mas ^{29}Si-NMR spectrum of uncured DC745U.

Variable contact-time cp NMR was used to study the cp dynamics of DC745U. The experiment involves the collection of a series of spectra where cp time is varied. The build-up curves of the dimethyl peak on the uncured sample take place at a slow rate and the maximum transfer is never observed within the time frame probed with longer polarization times possibly damaging to the equipment. The decay signal of the uncured Q sites (Si bonded to 4 oxygen atoms in the network, SiO_4) is less pronounced for the uncured material compared to the cured DC745U.

Cp driven ^{1}H/^{29}Si HETCOR NMR experiments were used to study the correlation of the dipolar couplings, resulting in a 2D roadmap identifying which ^{29}Si species and the ^{1}H species they are respectively coupled. For this experiment, the y-axis is the ^{29}Si dimension and the x-axis is the ^{1}H dimension. Only ^{29}Si signals participating in the cp are observed. The ^{1}H projection of the uncured DC745U sample shows a strong presence of a peak at 5.7 ppm that is assigned to hydrogen bonding of the silanol groups and a peak at 0 ppm that corresponds to methyl groups. No signal is observed in the region between 3 ppm and 5 ppm. The ^{29}Si-NMR projection shows a peak at -30 ppm that corresponds to phenyl groups. It also shows peaks between -85 ppm and -115 ppm that are associated to hydroxyl groups, water on the silica surface, and methyl protons of the polymer.

The HETCOR spectrum can be divided in four quadrants, as shown in Figure 5. The top left quadrant shows signals cross-polarized by water or hydroxyl groups. The top right quadrant shows peaks that are cross-polarized from methyl or vinyl groups. The bottom left quadrant shows signals that are cross-polarized by aromatic or hydroxyl groups on the silica surface. And the bottom right quadrant show peaks that are cross-polarized by methyl groups. While these quadrants give a measure of the degree to which the polymer can be polarized, they do not specify if the ability to polarize is due to entanglements, cross-linking, or the silica interface.

However, the experiment used long mixing time of 10 ms, which might explain the results. Often, a shorter mixing time gives better selectivity in terms of polarization and nuclei coupling. Experimental details for this section are described in Appendix III.

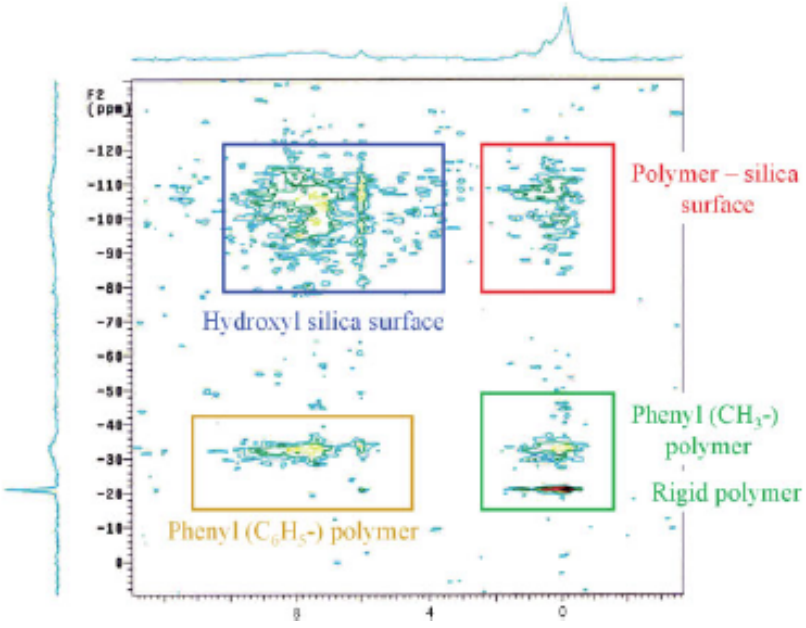


Figure 5. The 2D HETCOR $^{1}H/^{29}Si$ NMR spectrum for uncured DC745U.

1.3 Los Alamos National Laboratory[3]

^{1}H-, ^{13}C, and ^{29}Si-NMR spectroscopy were utilized to determine the composition of DC745U. The spectra are shown in Figure 6. The uncured material was stirred in $CDCl_3$ and centrifuged to separate the polymer from the filler. Results show that the extracted, uncured DC745U rubber contains approximately 98.8% of dimethyl siloxane monomers, less than 1% of methyl-phenyl siloxane repeat units, and less than 0.2% of vinyl siloxane repeat units. The ratio of vinyl groups to phenyl groups is 0.2: 1 in the resin. The ^{1}H-NMR spectrum shows peaks associated with phenyl groups (7.0- 7.7 ppm), vinyl groups (5.7- 6.2 ppm) and methyl groups (0 ppm). The ^{13}C-NMR spectrum shows peaks at 0 ppm and 130 ppm associated with methyl and phenyl groups, respectively. The ^{29}Si-NMR spectrum shows a peak at -22 ppm that corresponds to dimethyl siloxane groups in PDMS.

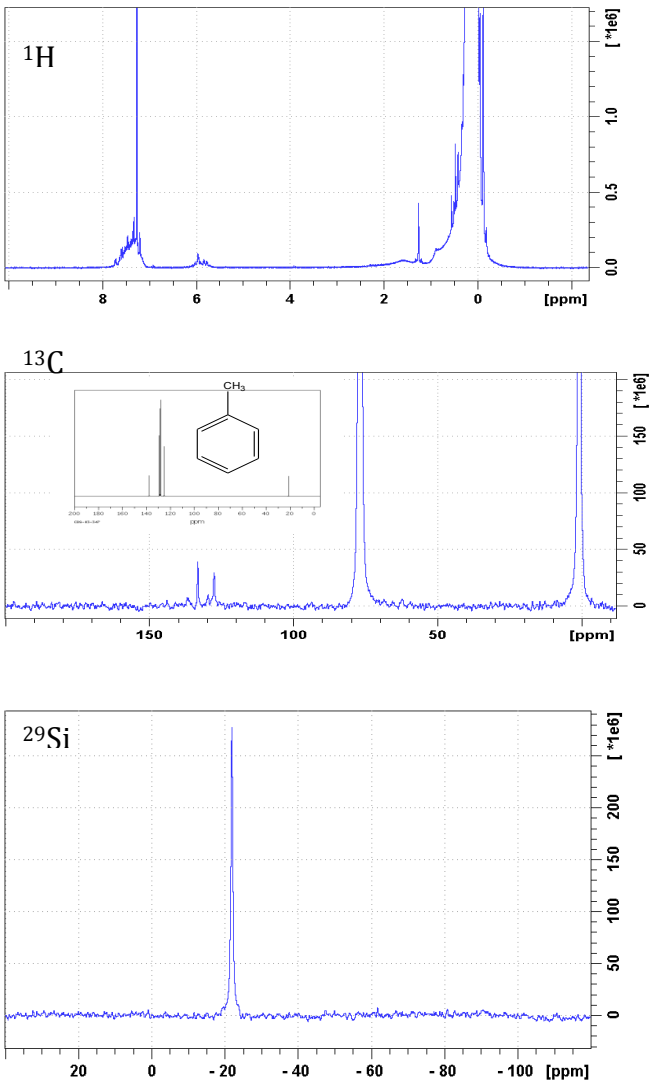


Figure 6. ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra for uncured DC745U.

A similar extraction of the uncured DC745U material was performed in toluene. The amount of filler in uncured DC745U was determined to be 38 wt%. The filler was analyzed by ^{29}Si-NMR spectroscopy and the spectrum shows a broad peak at -95 ppm and a sharp peak at -110 ppm, as shown in Figure 7. These peaks were assigned to amorphous silica and quartz, respectively. After deconvolution and fit of the peaks it was determined that the filler is composed of 33% quartz and 77% amorphous silica.

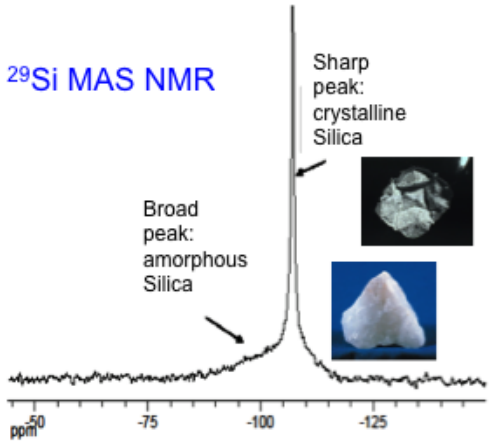
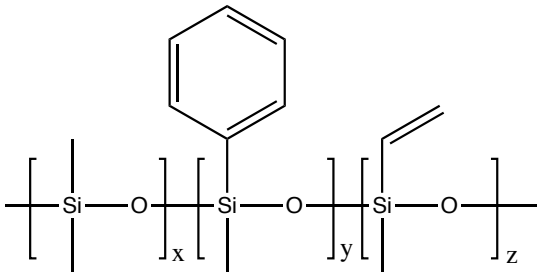


Figure 7. ^{29}Si-NMR spectrum of the DC745U filler.

1.4 Summary

^{1}H- and ^{29}Si-NMR has determined that uncured DC745U contains 97.5% dimethyl siloxane, 1.5% methyl-phenyl siloxane, and 1% of vinyl-siloxane (presumably *N*= 4) used as crosslinking sites, based on LLNL results. LLNL also determined that the amount if filler in the material is 30 wt. %. LANL determined that the composition of DC745U is 98.8% of dimethyl siloxane, 1% of methyl-phenyl siloxane, and 0.2% of vinyl siloxane repeat units, and the amount of filler is 38 wt%. Although these differences are not significant, they can have major impact in the materials properties. These compositional differences can be caused by changes to the formulation of DC745U during production. Because the formulation of DC745U is proprietary to Dow Corning, changes to its formulation are not notified to its customers. Figure 8 is a representation of DC745U uncured elastomer. Table 1 and 2 summarizes the work done on uncured DC745U by the different institutions and the chemical shifts of the peaks associated with DC745U, respectively.



LLNL	LANL
x = ≤100	x = ≤100
y = 1.5	y = 1
z = 1	z = 0.2

Figure 8. Relative composition of uncured DC745U.

Table 1. Work done by different institutions on DC745U uncured material.

	^{1}H	^{13}C	^{29}Si	^{1}H-MAS	^{13}C-MAS	^{29}Si-MAS	cp	MQ	^{1}H/^{29}Si HetCor
LLNL[1]	X	-	-	-	-	X	-	X	-
Washington and Jefferson College[2]	X	X	X	X	X	X	X		X
LANL[3]	X	X	X	-	-	-	-	-	-

Table 2. Chemical shifts assignment of peaks observed in ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra for uncured DC745U.

	^{1}H	^{13}C	^{29}Si
dimethyl	0	0	-20.5 - -22
phenyl	7.0-7.7	130	-32
vinyl	5.7-6.2	-	-
Isolated silanol	2	-	-
Water physisorbed to silica	4.1	-	-
Water exchange	4.9	-	-
Center of hydrogen bond of silanols	5	-	-
Geminal silanol	-	-	-80
Single silanol	-	-	-99
Siloxane	-	-	-109
quartz	-	-	-110

1.5 Recommended Further Work

Further studies on the composition and characterization of the peroxide initiator are needed. Currently, the peroxide initiator is procured as "buy by label" for production at Honeywell's Kansas City Plant. There are no acceptance requirements or defined methods for acceptance testing. Initiator characterization will help to define those requirements and methods. Additional work to fully characterize the filler in DC745U would also be helpful.

2.0 PART CURE PROTOCOL AND CURING STUDIES

2.1 Kansas City Plant (KCP)

2.1.1 Protocols for Milling, Molding/Curing and Postcuring DC745U Parts[4]

The DC745U gum is freshened by passing it through two rolls and rolling it into a cylinder while stripping from the front roll. The feeding is continued until the material has a smooth unbroken surface and appears to be virtually void-free. The gum cylinder is passed through the rolls and rolled into a loose, long, tapered cylinder by rolling the material at an angle while stripping from the front roll. The peroxide initiator is poured in small quantities (approximately 1/8 of the initiator) into the front of the cylinder, the sides are tapped to disperse the initiator, and the cylinder is passed through the mill rolls. This procedure is repeated until all of the initiator has been added to the gum. The method is finished by rolling the cylinder in the mill pan to pick up any initiator that has fallen out of the material while milling. This last step is repeated for a minimum of 10 times and until no catalyst is seen in the pan. The cylinder is divided into three equally sized pieces. Then, the gum is passed through the mill rolls lengthwise and a large smooth sheet is obtained.

[The roll milling protocol described above is specified in KCP work instruction procedure for production of 422104 Pressure Pad components.[4] *However, the protocol is not always conducted exactly as described in the procedure.]*

A template is used to cut two preforms of approximately 12.5 inches in diameter from the large flat sheet. Two 12.5 in. discs are laid on a clean polyethylene sheet and pressed down gently to remove trapped air. A fiberglass disc is placed on top of one 12.5 in disc and smoothed out. The other disc is placed on top of the fiberglass and smoothed out. The leftover rubber is passed through the mill rolls and rolled off into a large smooth sheet. Using a template, the sheets are cut out into two 6 in. diameter discs. Each disc is centered on top of a 12.5 in. preform. The preforms are placed on pre-heated molds.

[The preform/mat stacking protocol described above is specified in KCP work instruction procedure for production of 422104 Pressure Pad components.[4] *However, the protocol is not always conducted exactly as described in the procedure.]*

The preforms are gently pressed down to remove trapped air and degassed in the part mold. The materials are cured at 160 ± 15ºC for 1 hour and then allowed to

cool to 93 ± 50ºC for 45 min. The parts are removed from the mold and checked for soft spots, improper imbedded glass, broken ribs, and any other defects. The parts with no defects are trimmed and post-cured at 149ºC for 1 hour 15 minutes and 249ºC for 8 hours 30 minutes.

2.1.2 Other Curing Studies

In the early 1980s, KCP conducted studies on several different silicone elastomer/initiator combinations as candidates for pressure pad components.[5] The materials produced were Silastic E, 745U/101XL, and 745U/TS-50. The 745U/1001XL is produced from Silastic 745U (previous name for DC745U) crosslinked with Luperco 101XL and the 745U/TS-50 is Silastic 745U crosslinked with Cadox TS-50. The materials were cured as follow: Silastic E for 60 minutes at 93°C; 745U/101XL for 15 minutes at 171°C; 745U/TS-50 for 15 minutes at 116°C. Samples were post-cured as follows: Silastic E for 5 hours at 93°C; both 745U/101XL and 745U/TS-50 for 1 hour at 149°C and for 8 hours at 232°C.[5]

KCP also performed post-cure studies on Silastic E and 745U/101XL formulations. Samples of the materials were post-cured for different times and tested for hardness, solvent swell in toluene, and solvent extract. The results show that 745U/101XL is in general a better material for pressure pads because of its hardness, lower swelling in toluene, and less amount of extracts.[5] The data obtained for post-cure studies on 745U/101XL are tabulated in Table 3.

Table 3. Post-cure evaluations of 745U/101XL.

Sample	Oven cure (hrs @ °C)	Shore A-2 Hardness	Toluene swell ratio	Toluene extract (%)
745U/101XL	None	50	0.77	2.7
	1 @ 232	51	0.77	1.3
	2 @ 232	52	0.77	1.1
	4 @ 232	51	0.78	1.1
	6 @ 232	51	0.78	0.9
	8 @ 232	51	0.78	0.9

2.2 Lawrence Livermore National Laboratory

Samples were cured from Dow Corning DC745U silicone fluid with Luperox 101, Varox DBPH curing agent (2,5-dimethyl-2,5-di(t-butyl peroxy)hexane, 50% active, supported on $CaCO_3$). Additional control samples were obtained by varying the curing agent concentration. Curing was performed at 170°C for 10 min.

DC745U samples cured with different amounts of catalyst were analyzed using both NMR MOUSE and MRI (magnetic resonance imaging). The NMR MOUSE show that the T_2 relaxation time of the sample cured with $1/10^{th}$ the amount of the nominal catalyst is 20 ms lower, as shown in Figure 9.[1,6] NMR MOUSE parameters are described in Appendix IV.

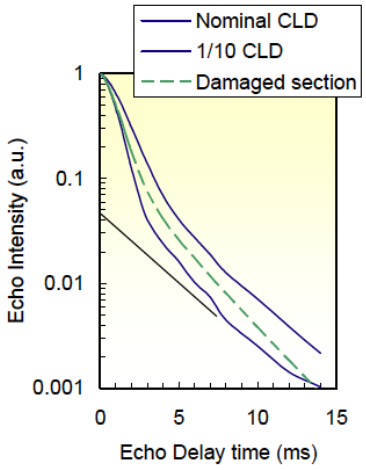


Figure 9. Spin-echo decay curves for different samples of DC745U.

MRI also shows differences in the relaxation time of samples cured with varying amounts of catalyst. 2D MRI shows higher signal intensity for the sample cured with 1/10th amount of catalyst, as shown in Figure 10.[6] Higher signal intensity translates to higher T_2, higher mobility of the network, and lower crosslink density. The sample produced with nominal amount of catalyst show lower signal intensity. Likewise, 3D MRI shows an increased in signal intensity going from nominal sample to the sample produced with 1/10th the amount of catalyst.[6] MRI experimental parameters are described in Appendix V.

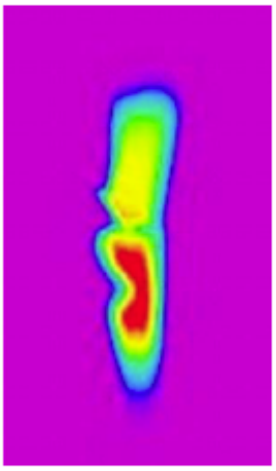


Figure 10. 2D T_2 weighted SPI MRI on two DC745U samples: top- nominal catalyst and bottom- 1/10th catalyst.

2.3 Summary

The curing and molding process of DC745U performed at KCP has been described in this section. The general procedure involves mixing the raw gum stock with the catalyst and curing at 160ºC for 1 hour and post-curing at 149ºC for 1 hour and at 249ºC for 8 hours.

Other curing studies were done at LLNL and involve production of DC745U materials using different amounts of initiator. These materials were analyzed by spin-echo NMR and MRI. Results show that materials produced with lower amount of initiator have lower crosslink density.

2.4 Recommended Further Work

Further studies are needed to insure that the initiator is being effectively incorporated into the DC745U during the roll milling process. If the milling process is inadequate or inconsistent, heterogeneous curing is possible and will impact part properties. The preform stacking method must also be evaluated to determine if it has an impact on the mat location and the properties of the final part. It is also important to understand the impact of post-cure conditions, if any, on full parts. NMR and other techniques will be very useful to probe changes in future studies.

3.0 CHARACTERIZATION OF CURED AND POST-CURED DC745U

3.1 Physical Properties

3.1.1 Solvent Swelling

LLNL determined the average crosslink density by solvent swelling studies in toluene.[1,7] The results show that the crosslink density is independent of the amount of peroxide initiator used until very small amounts are used (20% or less of the nominal initiator amount). The solvent swelling experiment is described in Appendix VI.

3.1.2 Bulk Density

The bulk densities for DC745U were found to be 1.291 g/cm^3 and 1.355 g/ cm^3 by Datapoint Labs[8] and Kansas City Plant[9], respectively. LANL determined that the density of DC745U is 1.2937 g/cc. The method for the determination of the density of DC745U performed by Datapoint Labs and Kansas City Plant are described in Appendix VIII[9] and IX,[10] respectively.

3.1.3 Oxygen Depletion and Evaporation Rates of Water Droplets[11]

These studies were performed to determine how much time is required to remove oxygen and water present in DC745U materials. Assuming the external mass transfer resistance is negligible, it will take approximately 84 minutes to remove 99% of the sorbed oxygen from the DC745U materials after it is exposed to an oxygen free atmosphere. Water sorbed in the rubber will also be removed in this time frame, but water desorbing from the silica filler particles will take longer. It was also estimated that 13 and 30 microliter droplets initially lose about 4.4% and 3.7% of their mass per minute, respectively. It was estimated that it would take 30 minutes to completely evaporate the 13 microliter droplet and over 2 hours to evaporate the entire 30 microliter drop in a dry environment.

3.2 Spectroscopic Analysis

3.2.1 NMR

3.2.1.1 Lawrence Livermore National Laboratory

LLNL performed NMR studies on cured DC745U extracts in CD_2Cl_2.[1] The spectrum shown in Figure 11 shows the disappearance of various peaks between 7–8 ppm and 6 ppm when compared to the spectrum of the DC745U gum stock in Figure 1B. Several peaks between 0 and 0.5 ppm also disappeared.

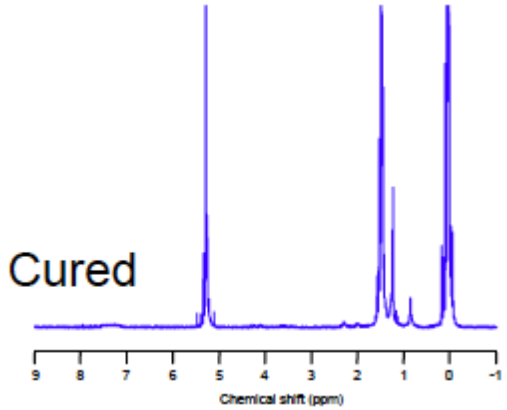


Figure 11. Solution state ^{1}H-NMR spectrum of cured DC745U extracted in CD_2Cl_2.

3.2.1.2 Los Alamos National Laboratory

^{1}H- and ^{13}C- MAS NMR performed on cured DC745U samples show peaks associated with methyl groups (0 ppm on both NMRs) and phenyl groups (7 ppm and 125–140 ppm, respectively).[12] ^{29}Si- MAS NMR shows peaks associated with phenyl groups (-31 to -35 ppm), methyl groups (-22 ppm) and silicate and quartz between -100 and -115 ppm. The MAS/NMR spectra are shown in Figure 12.

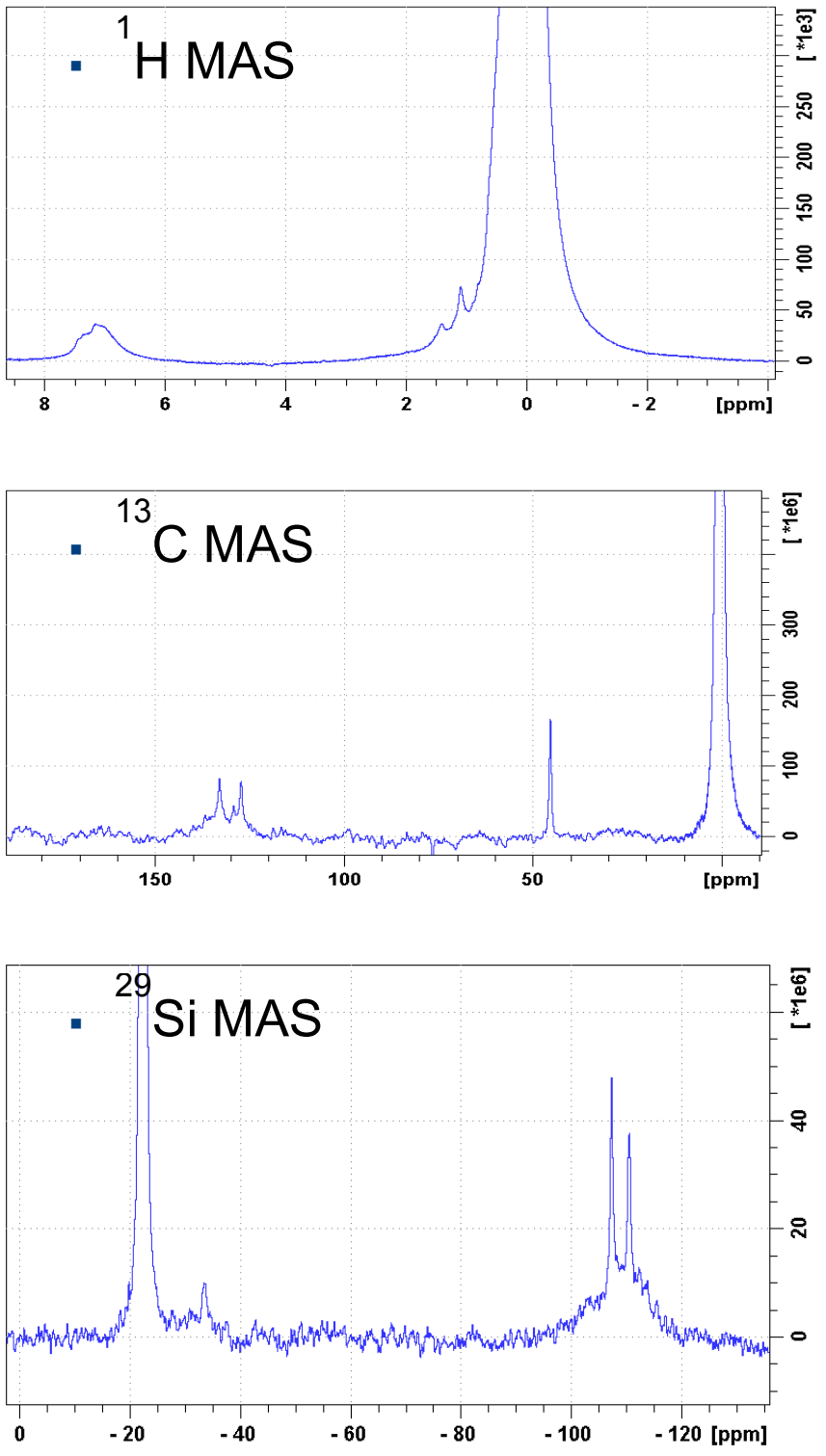


Figure 12. ^{1}H-, ^{13}C-, and ^{29}Si- MAS NMR spectra for cured DC745U.

3.3 Thermal properties

3.3.1 Lawrence Livermore National Laboratory

DMA and DSC (Figure 13A and 13B, respectively) studies show that DC745U crystallizes at approximately -45°C. The DSC thermogram shows two glass transition temperature at -90 and -130°C.[1] The crystallization rate was observed in isothermal DMA (Figure 13C) studies at -40°C and shows that the change in bulk response due to an increase in crystallinity levels off after approximately 1 hour. The procedures for DSC and DMA are described in Appendix VIII. It was also determined that the sample made with 1/10 the amount of catalyst and with lower crosslink density has a lower % crystallinity and warmer crystallization temperature as can be observed in Figure 14.[1] Samples made with the nominal and ½ the amount of catalyst showed the same crystallization temperature.

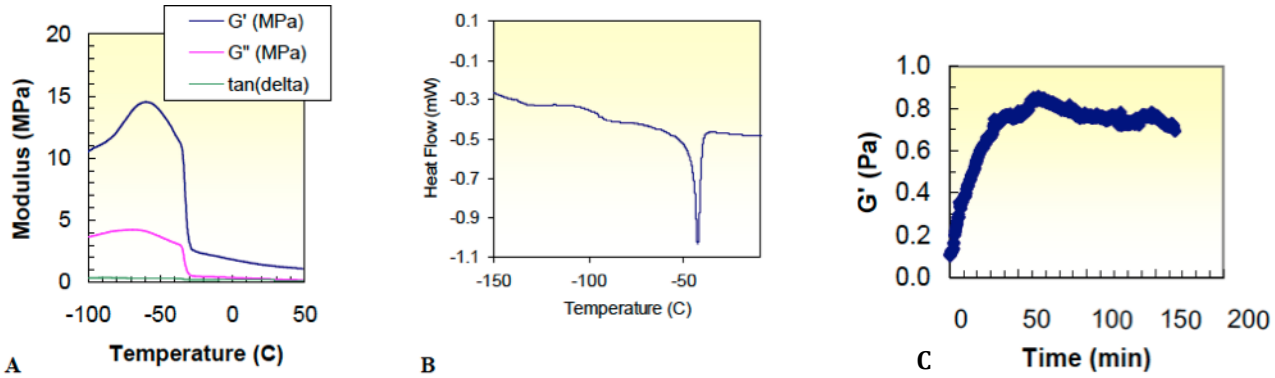


Figure 13. DMA (A) and DSC (B) studies of DC745U. Isothermal DMA at -40°C (C).

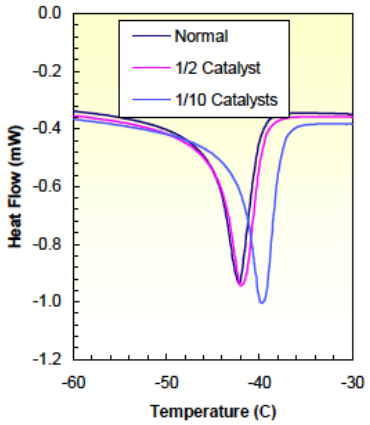


Figure 14. DCS thermograms of DC745U produced with different amounts of catalyst.

3.3.2 Los Alamos National Laboratory

DSC data shows that DC745U crystallizes at temperatures between -46 and -56°C.[13] DMA shows that the crystallization of the material is more evident at -52°C.[13] Figure 15 shows the DSC and the DMA thermographs for DC745U. In addition, TGA analysis show that the onset degradation temperature for DC745U is ~ 510ºC and a total weight loss of ~ 55%.[14]

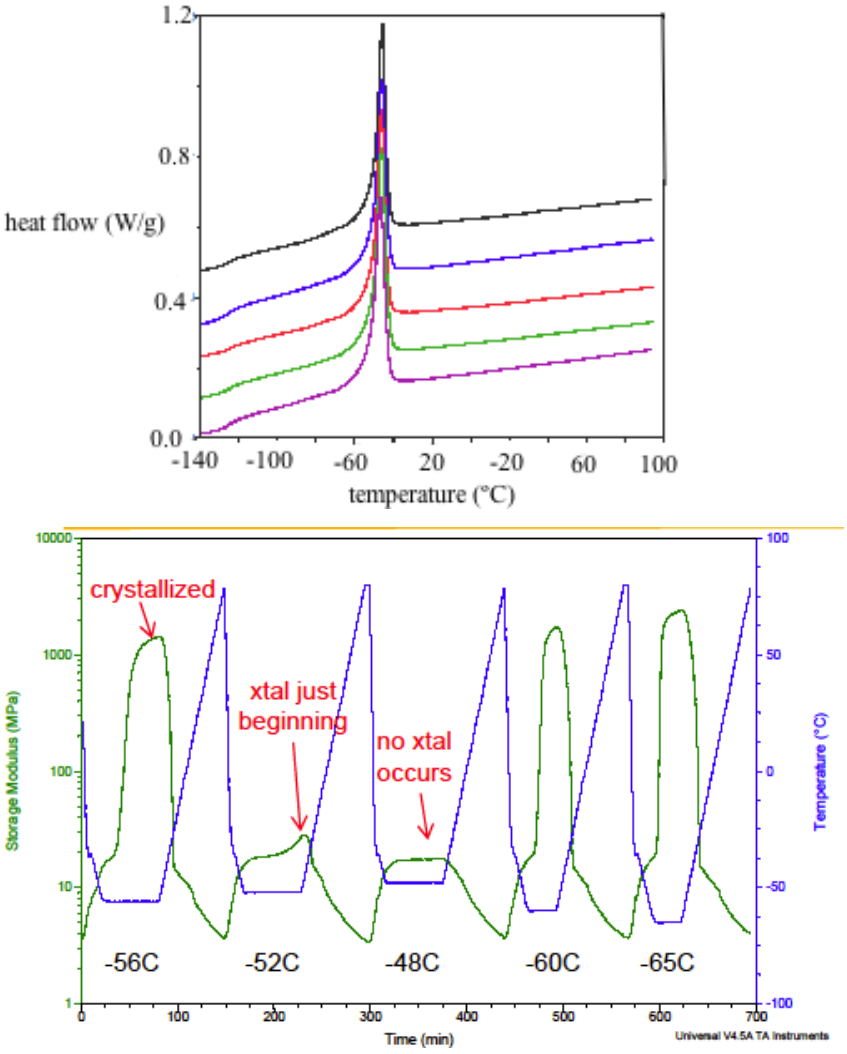


Figure 15. DSC for multiple DC745U samples (top) and DMA (bottom) thermograms of DC745U.

3.4 Mechanical properties

3.4.1 Tensile Properties

3.4.1.1 DataPoint Labs

DataPoint Labs performed tensile tests on DC745U and the results are summarized in Table 4. At room temperature, Datapoint Labs shows that DC745U material has an ultimate strain of approximately 271% at an engineering stress of 5.18 MPa.[8] The material reaches the yield point at a strain of

approximately 20%. At the yield point the material deforms permanently until it reaches the ultimate strain point after which the material fractures. Datapoint Labs also performed tensile test at -54°C and 71°C but was unable to obtain ultimate strain values because the extensometer reached its limit before the sample fractured. The method used for tensile tests is described in Appendix X.

3.4.1.2 Lawrence Livermore National Laboratory

LLNL reported a stress of 141 psi at a stretch ratio of 1.41 and 20% elongation at room temperature.[15] The method used for tensile tests is described in Appendix XI.

Table 4. Tensile Properties of DC745U.

	Temperature °C	Tensile strength MPa	Ultimate strain %	Stress PSI	Stretch ratio
LLNL[15]	24[a]	-	-	141[b]	1.41[b]
Datapoint Labs[8]	24	5.18	271	-	-
	-54[c]	0.83[c]	47.2[c]	-	-
	71[c]	1.03c	56.4[c]	-	-

[a] Temperature was not specified in the manuscript and was assumed.
[b] Values reported were at a maximum elongation of 20%.
[c] Maximum values obtained before the extensometer reached its limit before the sample fracture.

3.4.2 Compressive Properties

3.4.2.1 Datapoint Labs

Datapoint Labs performed compressive tests on DC745U at different temperatures.[8] Data shows that at room temperature and at 71°C the material undergoes fast stiffening after 40% strain and it fractures before reaching the yield point. At these temperatures, DC745U reaches an ultimate stress of 11.5 MPa at approximately 65% strain. At a temperature of -54°C, DC745U reaches a yield point at a strain between 5-12% after which the material deforms permanently. The material reaches an ultimate stress at a strain between 43-49%. Results are summarized in Table 5. The method used to measure compressive strength is described in Appendix XII.

Table 5. Compressive Test results of DC745U at different temperatures and loading rates.

	Rate (load/s)	Temperature (°C)	Stress[a] (MPa)	Strain[b]	Yield (stress/strain)
Datapoint Labs	-	23	11.5	65%	-
	-	-54	11.5	43-40%	3-5/5-12%
	-	71	11.5	65%	-
LANL	0.001	-75	23	0.16	18/0.1
		-40	2	0.64	-
		-20	1.35	0.64	-
		0	1.5	0.61	-
		20	1.45	0.60	-
	0.01	-75	40	0.39	23/0.03
		-50	1.8	0.40	-
		-40	1.8	0.40	-
		-20	1.8	0.40	-
		0	1.8	0.40	-
		20	2	0.40	-
	0.1	-75	23	0.56	16/0.12
		-50	1.82	0.63	-
		-40	1.81	0.61	-
		-20	1.52	0.60	-
		0	1.52	0.60	-
		20	1.52	0.60	-

[a] Datapoint Labs reports engineering stress and LANL reports true stress.

[b] Datapoint Labs reports engineering strain and LANL reports true strain.

3.4.2.2 Los Alamos National Laboratory

LANL performed compressive tests on DC745U at different temperatures and loading rates.[13,16] At a rate of 0.1/s, results show that moderate stiffening is observed at temperatures of -40°C and -50°C as shown in Figure 16. Cyclic loading experiments at a load rate of 0.01/s show a major change in compressive modulus from -50°C to -75°C. Additionally, major damage to the network structure is observed with cycling and this damage is amplified at colder temperatures.

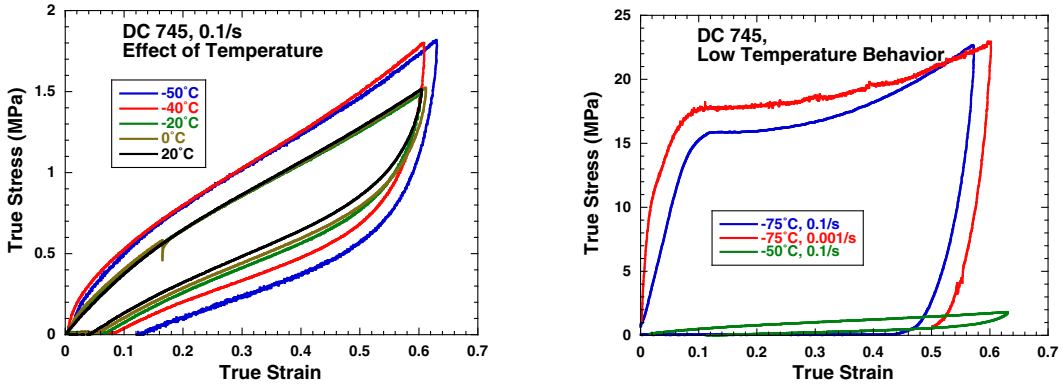


Figure 16. Compressive tests results on DC745U at a load rate of 0.1/s. The dwell time before testing was ~ 5 minutes. Longer dwell times would show a crystalline transition at -50ºC.

In general, similar compressive behaviors are observed for samples at temperatures of -20°C, 0°C, and 20°C and loading rates of 0.1/s, 0.01/s, and 0.001/s. At a rate of 0.01/s samples analyzed at temperatures of -50 and -40°C show similar behaviors than samples analyzed at temperatures between -20 and 20°C. Samples analyzed at -50 and -40°C and at rates of 0.1/s and 0.001/s show increased in stiffening. Only DC745U samples analyzed at -75°C show yield points. The yield point is at higher stress and lower strain for the experiment performed at a loading rate of 0.01/s. Results are summarized in Table 5. The method used to measure compressive strength is described in Appendix XIII.

3.4.2.3 Kansas City Plant

In the early 1980s, KCP used compressive properties to compare several different silicone elastomer/initiator combinations as candidates for pressure pad components.[5] The materials analyzed were two lots of Silastic E, 745U/101XL (Silastic 745U crosslinked with Luperco 101XL), and 745U/TS-50 (crosslinked with Cadox TS-50). The samples were place in test fixtures and compressed to 30% strain for long-term storage and periodic testing. The samples were also stored in the fixtures at different temperatures.[5] Results for 745U/101XL are summarized in Table 6. The 745U/TS-50 samples suffered nearly twice as much stress loss as the other samples and 745U/101XL exhibited 10-15% better stress retention than either lots of Silastic E. The stress retention of one sample of each group was measured for the second time at the end of 112 days of storage. Data shows that little changed had occurred in the samples tested, except for 745U/TS-50.

Table 6. Stress Relaxation Tests Results by KCP.

Material formulation	Sample number	Storage temperature (°C)	Stress retention %	
			After 365 days	After 112 days
745U/101XL	6	RT	70	-
	7	55	67	-
	8	55	61	-
	9	75	58	-
	10	75	63	63
	20	55	54	-
	21	75	49	-
	22	75	46	41

Visual observations[5] of the samples at the end of the stress relaxation measurements show that 745U/TS-50 underwent a severe permanent deformation and exudate visible in grooves. Both lots of Silastic E show slight permanent deformation and traces of exudate. The 745U/101XL sample showed no visible permanent deformation and exudate.

3.4.3 Pressure Volume Temperature (PVT)

PVT data are equation-of-state thermodynamic properties that describe the compressibility and volumetric expansion of the material.[8] Dilatometry is used to measure the change in volume of a specimen subjected to different temperatures and pressures. Appendix XIV describes the method used to measure PVT. The PVT data obtained by Datapoint Labs for DC745U is shown below:

Pressure-Volume-Temperature Data

Specific Volume cm3/g

Temp	Pressure MPa					
°C	0	40	80	120	160	200
33	0.7837	0.7619	0.7458	0.7334	0.7233	0.7142
43	0.7885	0.7665	0.7494	0.7367	0.7262	0.7168
53	0.7935	0.7696	0.7523	0.7391	0.7283	0.7188
74	0.8045	0.7777	0.7588	0.7447	0.7334	0.7233
178	0.8660	0.8198	0.7931	0.7746	0.7603	0.7479
253	0.9207	0.8533	0.8194	0.7975	0.7810	0.7670

Volumetric Stress-Strain Data

Volumetric Strain %

Temp	Volumetric Stress MPa					
°C	0	40	80	120	160	200
33	0.0000	2.7880	4.8324	6.4246	7.7076	8.8687
43	0.0000	2.7899	4.9600	6.5767	7.9080	9.0935
53	0.0000	3.0115	5.1932	6.8491	8.2193	9.4133
74	0.0000	3.3326	5.6765	7.4319	8.8400	10.0925
178	0.0000	5.3317	8.4226	10.5520	12.2094	13.6427
253	0.0000	7.3204	11.0053	13.3794	15.1720	16.6956

Bulk Modulus

Bulk Modulus MPa

Temp	Volumetric Stress Range MPa				
°C	0 - 40	40 - 80	80 - 120	120 - 160	160 - 200
33	1435	1956	2512	3118	3445
43	1434	1843	2474	3004	3374
53	1328	1833	2416	2919	3350
74	1200	1707	2279	2841	3194
178	750	1294	1878	2413	2791
253	546	1086	1685	2231	2625

3.4.4 Equation of State (EOS)[13]

Shock compression data on DC745U did not exist prior to this study. To interrogate the influence of crystallization on the shock properties of DC745U, two sets of low velocity plate impact experiments were performed using the LANL single stage large bore (78 mm) gas gun at Chamber 9. Using embedded electromagnetic gauges, four plate impact experiments were performed on a target configuration of 2 layers of DC745U, backed by PMMA at -55°C and room temperature. The samples were cooled to -60 to -80°C and held for 1 hr to ensure complete crystallization per the DMA crystallization studies by Orler,[13] above. At ~ -52°C, the polymer crystallizes with a % crystallinity of ~ 40%. The presence of quartz in the material resulted in significant electrical noise on the embedded gauges. Figure 17 shows Hugoniot data from the room temperature and cold low velocity impact experiments. The density of the DC745U increases by ~ 10%[1,13] upon crystallization and cooling to -55°C. These experiments are the first cold plate impact experiments on polymers. From the data, it is apparent that crystallization results in an increase in the shock velocity by ~ 1.5x and associated decrease in particle velocity associated with an increase in the shock impedance of the material.

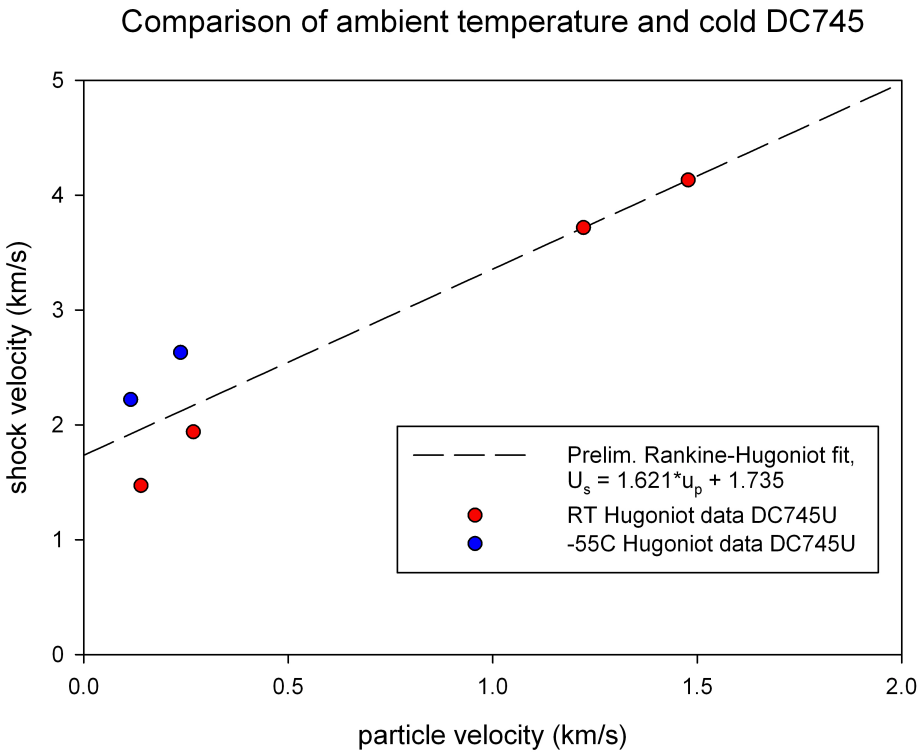


Figure 17. Summary of Hugoniot data for DC745U. The two new points are shown at higher particle velocity in red.

Due to the electrical noise derived from the shocked quartz filler, two additional cold experiments were attempted using photon Doppler velocimetry probes at the impact interface and rear windowed surface of the sample to measure the shock velocity. However, this method was not adequate for measuring the Hugoniot loci due to contraction of the material. In addition, impedance matching is challenging in this configuration due to the low impedance of the DC745U.

Two additional Hugoniot points at room temperature were obtained from front surface impact experiments. In these experiments, DC745U was affixed to the front of Lexan projectiles and impacted into oriented LiF windows. Particle velocity wave profiles were measured at the DC745U/LiF interface using dual VISARs. The Hugoniot loci were determined using the measured particle velocity, projectile velocity, and impedance matching methods. Figures 18 and 19 show the interfacial particle velocity wave profiles from the two experiments.

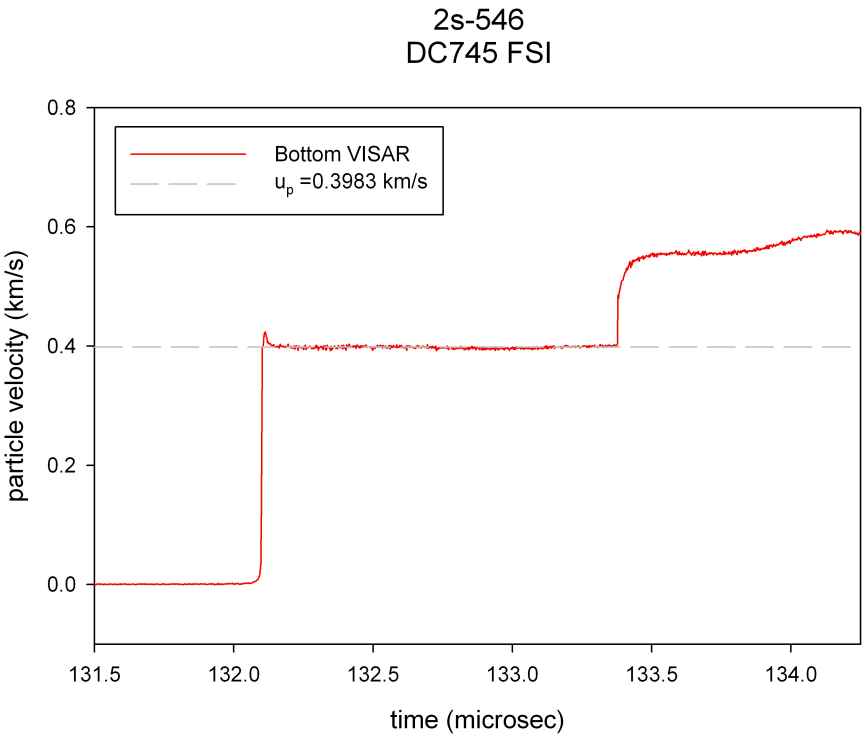


Figure 18. Shot 2s-546, DC745U impacting LiF at 1.620 km/s. There is evidence of relaxation on the front of the shock wave at the DC745U-LiF interface.

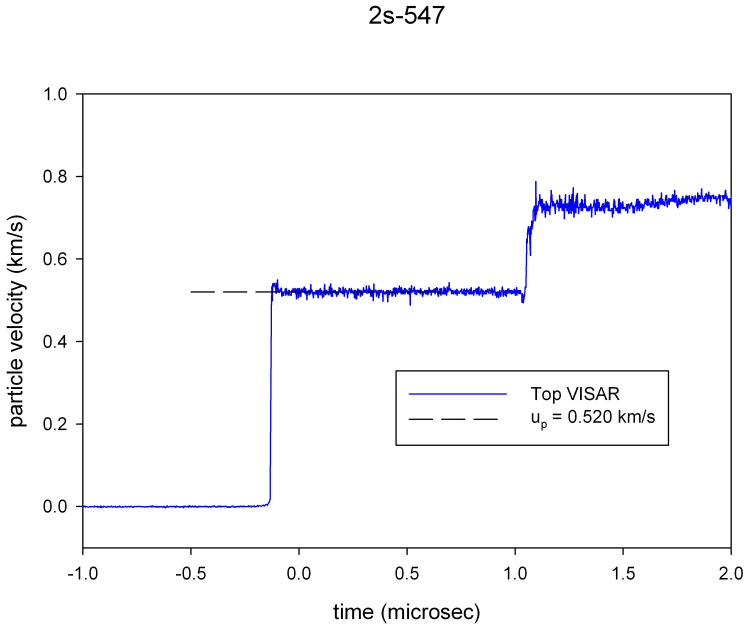


Figure 19. Shot 2s-547, DC745U impacting LiF at 1.998 km/s. Lowered light levels at impact due to polymer filler resulted in noisy profiles. There is evidence of a relaxation process or skin effect at the front of the wave profile similar to 2s-546.

In both experiments, a decay in the initial particle velocity is observed at the interface. This is likely due to viscoelastic effects, with the decay related to viscoelastic relaxation from the "instantaneous" to "equilibrium" Hugoniot. Additional experiments are underway to interrogate the relaxation time scale as a function of shock input pressure and strain rate. From the 4 measured Hugoniot points for DC745U, the room temperature unreacted Hugoniot can be approximated by the linear Rankine-Hugoniot fit to the data in the shock velocity-particle velocity plane: $U_s = 1.621 + 1.735\ u_p$. The two lowest pressure points are not included in the fit, and fall off of the linear Rankine-Hugoniot fit at low pressures (particle velocities) consistent with other polymers and organic materials due to compaction of free volume in the polymer network at low shock pressures. These data can be compared with Hugoniot data for similar polymers such as high density (1.1 g/cm^3) S5370 and SX358, Sylgard 184 (1.05 /cm^3), and liquid PDMS (<1 g/cm^3).

3.5 Summary

Cured and post-cured DC745U were characterized using the techniques described in Table 7. DC745U was cured using different amounts of catalyst. These materials were analyzed by solvent swelling, DSC, and spin-echo NMR experiments (described in the previous section). Results show that the amount of catalyst used to cure DC745U becomes important only when very small amounts are used (20% or less of the nominal initiator amount). The NMR spectra for the cured and uncured materials show no significant differences. DSC shows that DC745U crystallizes at approximately -46 ºC. Compressive tests show that crystallization of DC745U does have an influence on compressive response. DC745U undergoes a moderate stiffening at temperatures between -40 and -50ºC and a major change in compressive modulus at temperatures between -50 and -75ºC. Softening of the material becomes visible under cycling and this damage is amplified at cold temperatures.

Table 7. Work done by different institutions on cured DC745U.

	Solvent swelling	Bulk density	NMR	DSC	DMA	Tensile strength	Compressive strength	PVT
LLNL	X [1,7]		X [1]	X [1,13]	X [1,13]	X [11]		
LANL		X	X [1,12]	X [10]	X [10]		X [10, 12]	
KCP		X [8]					X [4]	
Datapoint Labs		X [8,9]				X [8,15]	X [7]	X [8]

3.6 Recommended Future Work

A better understanding of low temperature mechanical behavior of cured DC745U is very important to our understanding of mechanical response in relevant weapon environments. Additional low temperature mechanical characterization is needed with a focus on "soak time" at low temperature weapon environments.

Mechanical data should be coupled with isothermal DMA crystallization kinetics studies at low temperature. Thermal cycling studies are also need to understand the material's response over the entire temperature range of the weapon environment. New studies should address any new data that may be needed to improve system, component and material models and validation of those models.

Additional EOS work is needed (and currently in progress). Two cold shots have been assembled, designed to use PDV as the principal diagnostic of shock velocity in the material at cold temperatures. Furthermore, the cold target cell design has been re-worked for better insulation and cooling capability. The first prototype of the new design is being machined presently.

4.0 AGING STUDIES

4.1 Stockpile aged/Surveillance/Returned Parts

4.1.1 Lawrence Livermore National Laboratory

LLNL performed a series of studies on DC745U parts used in two major components in the W80: aft cap support (ACS) and outer pressure pad (OPP). The materials were obtained from Kansas City Plant as 1 cm x 1 cm samples.[1]

ACS surveillance tests done at LLNL comprised of measuring a secant modulus at two different segments of the compression/deflection tests.[1] Results on the ACS samples show a large amount of scatter but no significant trend with service time as shown in Figure 20. This indicated that the scatter is due to testing variances associated to the testing method itself, or variations due to sample dependent differences.

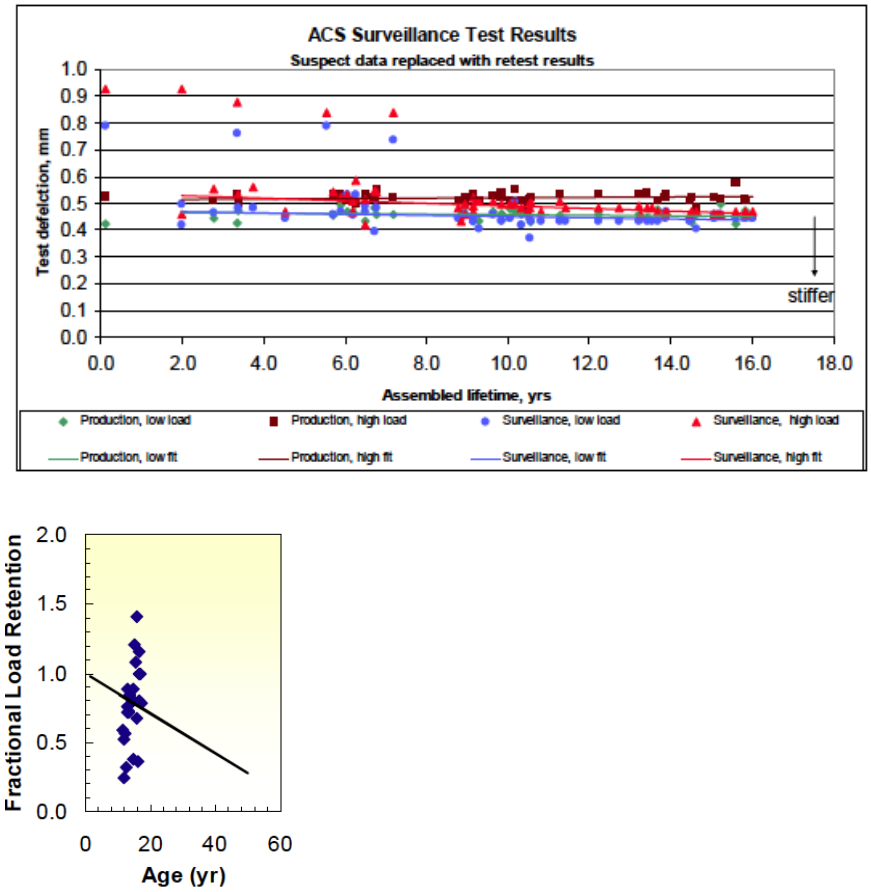


Figure 20. Surveillance testing results on Aft Cap Support (top) and Outer Pressure Pads (bottom).

OPP surveillance testing comprised of compression tests in which the load is determined at two different compressed thicknesses.[1] Results on OPP parts show more scatter than ACS samples. *LLNL suggested that a linear regression fit of OPP data predicts load retention of 25% at 50 years, Figure 20.* In reality, these tests provided little information on the materials and are inadequate for predicting the lifetime of both ACS and OPP samples.

LLNL also performed high resolution NMR, NMR MOUSE, and MRI experiments on damaged and undamaged DC745U pads that were used in service.[6] Decay curves obtained from traditional spin echo NMR analysis were characterized by two components relaxation functions, with shorter decays (low T_2) representing network polymer chains and longer decays (high T_2) representing mobile non-network sol fractions and dangling ends (Figure 21).[6] The curves also indicate that while the sol fraction seemed to increase in the damaged pad, a slight change in rate occurs in the more rapidly decaying sections representing the less mobile portion of the polymer network. The values obtained for transverse relaxation times T_{2e} were 2.11 ms for the undamaged pad and 2.16 ms for the

damaged pads. These values suggest that the damage is occurring in the more mobile sol component of the polymer. By quantifying the residual dipolar couplings the T_2 relaxation times were determined to be 4.91 ms for the undamaged pad and 5.18 ms for the damaged pad. Residual couplings were 677.7 Hz and correlation time of 17 ms for the undamaged pad and 595.7 Hz and 2.12 ms for the damaged pad. The relative fraction of the slow component increased in the damaged samples suggesting that the damage causes a decrease in the fraction of the immobile phase either by chain scission or by reduction in the number of entanglements in the immobile phase. ^{1}H-NMR transverse relaxation time experiments performed on surveillance return OPP parts aged on service for different times[1] show that the crosslink density is unchanged with time. The data shows that OPP parts do not undergo any significant changes when aged on service.

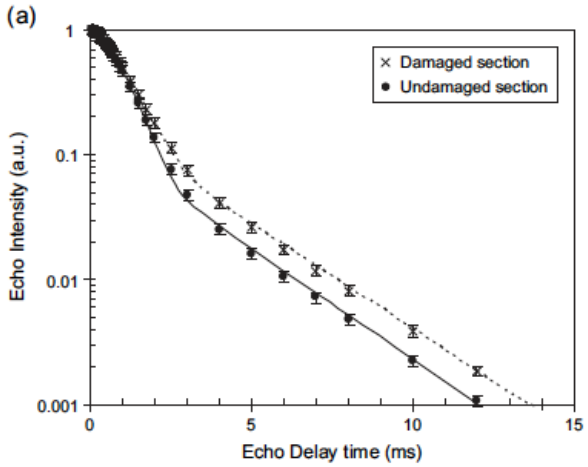


Figure 21. Echo decay curves with high field data points and T_2 curves (dashed= damaged; solid= undamaged).

NMR MOUSE experiments[6,17] also show changes in the T_2 relaxation times on damaged and undamaged parts that are more distinct on the top of the pads. The damaged pad has a T_2 relaxation time of 75 ms and the undamaged pad has a T_2 of 95 ms. MRI experiments where characterized by lower T_2 values on undamaged pads.[6] MRI data confirms that the damaged pad, after service, can be described by the heterogeneities in the mobility of the polymer network through the pad.

Similar observations on T_2 relaxation behaviors were observed on DC745U OPP samples.[1] Based on LLNL observations, approximately 20% of OPP parts contain a small region of permanent deformation characterized by lower thickness, distorted rib shapes, and curling. The damaged region is characterized by a slower relaxation time of T_2 = 0.9 ms (undamaged T_2 = 1.01 ms) for the network species and an increased contribution of X_{sol} = 0.15 (undamaged X_{sol} = 0.05) due to the non-network sol fraction, based on NMR ^{1}H spin echo experiments on NMR MOUSE.

4.1.2 Los Alamos National Laboratory

LANL surveillance testing was conducted on returned B61 pressure pad components. Surveillance testing consists of a total load measurement on the part. The load is measured at both low and high strain. Significant scatter is observed in the data, especially at high strain rates, as shown in Figure 22.

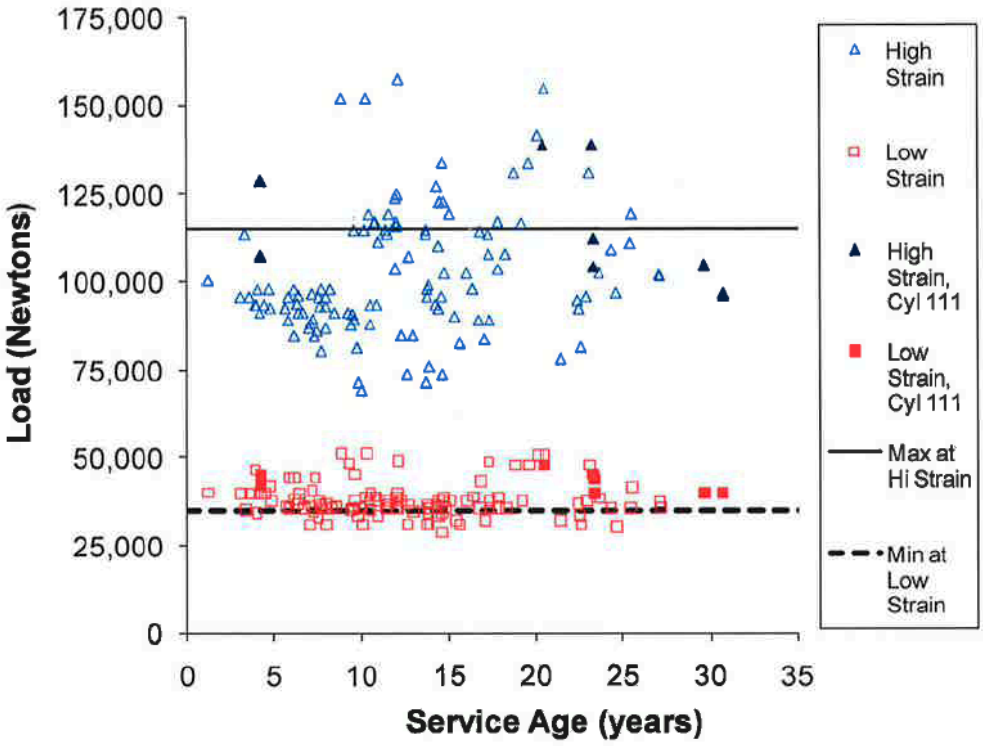


Figure 22. Surveillance testing on B61 pressure pad components.

LANL also conducted spectroscopic analysis on samples from surveillance parts. The samples were obtained from parts aged in service that were 20 to 27 years old. Original part molding conditions were 171°C for 35 minutes, post-cured at 149°C for 1 hour, and 249°C for 8 hours.[18] The samples were extracted with $CDCl_3$ and the extracts were analyzed using ^{1}H-NMR spectroscopy. Differences in the spectra for different samples of similar age were observed even though all samples were treated in the same way (Figure 23). The differences could be due to heterogeneities of the pads. The solid-state NMR shows typical ^{1}H and ^{29}Si MAS NMR spectra for DC745U.

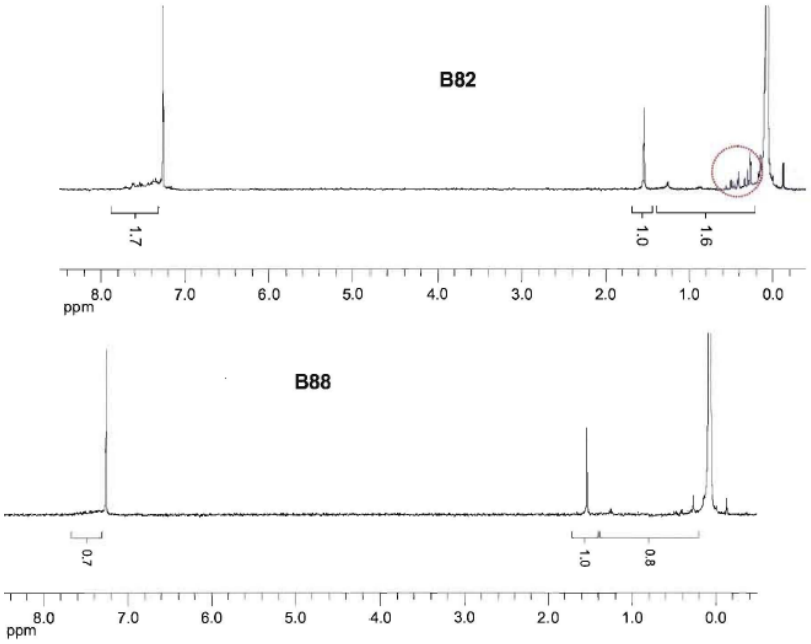


Figure 23. ^{1}H-NMR spectra for extracted material obtained from two different DC745 Samples.

4.2 Accelerated Aging- Thermal

4.2.1 Lawrence Livermore National Laboratory

SPME (solid phase micro extraction) GC/MS was the technique utilized by LLNL to study thermal degradation of DC745U. The samples were heated for two weeks at 70°C prior to analysis. Two main degradation products were observed using this technique: linear and cyclic siloxane species resulting from postulated thermally activated backbiting mechanism illustrated in Appendix XIX. Other products observed were benzene, branched hydrocarbons, siloxanes, metal alkyl additive, dihydroperoxide, and large hydrocarbon species. Degradation products are listed in Table 8. The methodology used for this experiment is described in Appendix XVIII.

Table 8. Major offgassing species from DC745 when heated to 70°C for 2 weeks.

Raw gum stock		Cured DC745	
Retention times (min)	**Product**	**Retention times (min)**	**Product**
2.97-3.3	Benzene	3-3.3	Benzene
6.8-7.8	Branched hydrocarbons	4.8	Siloxane
8.8	Siloxane	8.8	Siloxane
10.2	Metal alkyl additive	9.4	Metal alkyl additive
10.8	Dihydroperoxide	10.2	Metal alkyl additive
12.17	Large (C> 20) hydrocarbon	-	-

4.2.2 Los Alamos National Laboratory

Compression set was measured for all accelerated aged samples and results are shown in Figure 24 and Table 9.[18] Results demonstrate that samples show large compression set and the most important factor was aging temperature. Samples aged at 120°C show higher compression set than samples aged at 80°C. This means that DC745U samples aged at higher temperatures are less likely to resist permanent deformation. Humidity does not seem to contribute in the large values of compression set of the samples. The aging conditions are described in Appendix XV.

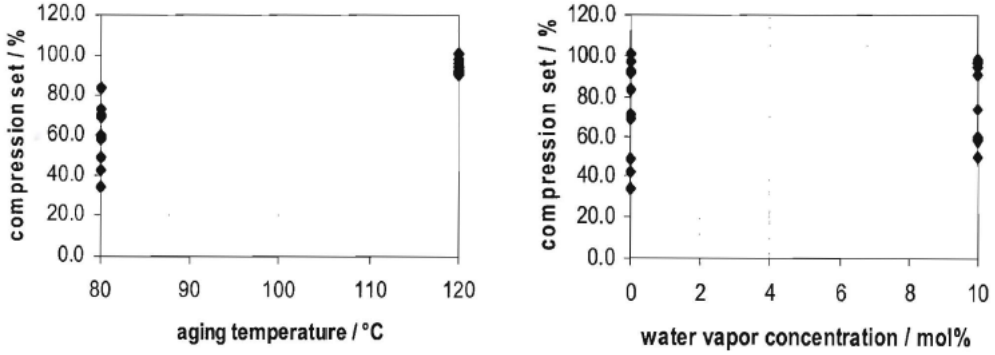


Figure 24. Compression set as a function of temperature and humidity level for accelerated aged DC745U materials.

Table 9. Compression set results for thermally aged DC745U samples.

Aging conditions:				% compression set
Curing	% water	% oxygen	Temperature (°C)	
No post-cure	10	0	120	104.375
No post-cure	10	10	120	108.696
Post-cure	0	0	120	104.965
Post-cure	10	0	120	97.872
No post-cure	10	10	80	63.889
Post-cure	0	10	80	36.879
No post-cure	0	0	80	77.778

T_2 relaxation time experiments were also performed on thermally aged DC745U samples.[19] The samples used in these studies were already post-cured during molding and assembly. The aging process involved heating the sample in air at 250°C for different times: 2, 3.5, 18.5, 41.5, and 59.5 hours. A sample aged for 59.5 hours and an un-aged sample were hydrated at 100% humidity and room temperature for 3 weeks. Results show that the sample aged for 3.5 hours has a similar decay behavior to the sample aged for 2 hours and the samples aged for 18.5, 41.5, and 59.5 exhibit the same relaxation decays but faster than the previous two samples, as shown in Figure 25. Faster relaxation times imply that the samples are becoming stiffer probably because of the material's release of adsorbed water from the surface of the filler. When the material releases adsorbed water there is a stronger interaction of the polymer with the filler surface. When the aged sample was hydrated for 3 weeks, the relaxation decay was the same as for the dehydrated sample. This observation implies that once the adsorbed water has been released the polymer chains are irreversible adsorbed by the filler. This data is shown in Figure 26.

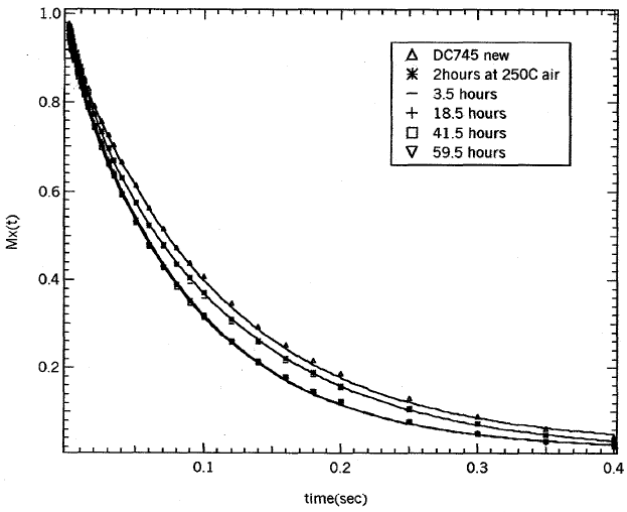


Figure 25. Transverse magnetization decay curve for DC745U samples aged for different periods of time.

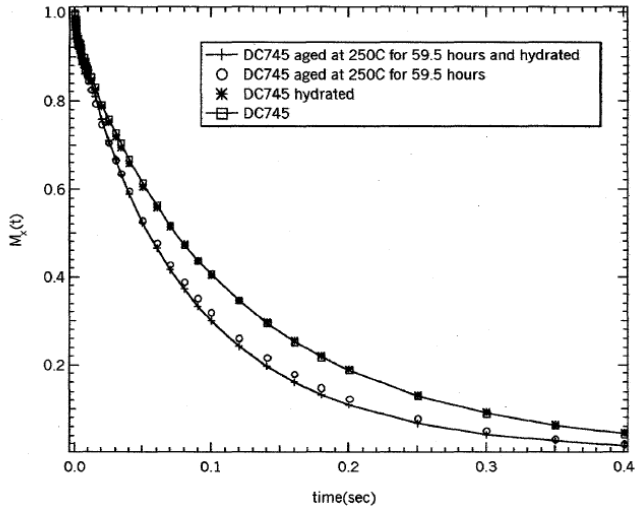


Figure 26. Transverse magnetization decay curves for dehydrated and hydrated samples of aged DC745U.

4.2.3 Summary Table

Table 10. Summary of work done on thermally aged DC745U samples.

Institution	Time of aging	Temperature (°C)	Method
LLNL	2 weeks	70	SPME GC/MS
LANL	6 months	80 and 120	Compression set
LANL	2, 3.5, 18.5, 41.5, and 59.5 hours	250	NMR spectroscopy (T_2s)

4.3 Accelerated Aging- Radiolytic

4.3.1 Lawrence Livermore National Laboratory

Multiple Quantum (MQ) NMR methods are more selective to network dynamics and structure.[1,7] MQ growth curves for 5, 50, and 250 kGy radiative aged samples show that the growth rate is dose dependent with higher exposure leading to higher growth rates (Figure 27). Results show that the network is dominated (89% of monomers) by low residual dipolar couplings near 700 rad/s at low doses of radiation, likely due to the general network polymer chains. The remaining network monomers are in a domain with significantly higher residual dipolar coupling near 3200 rad/s due to polymer chains that are physically or chemically interacting with the silica filler surface or in a domain with significantly higher crosslink density than the dominant network chains. Data suggests that the radiation causes an increase in crosslink density in the polymer network and an increased interaction of the polymer chains with the filler.

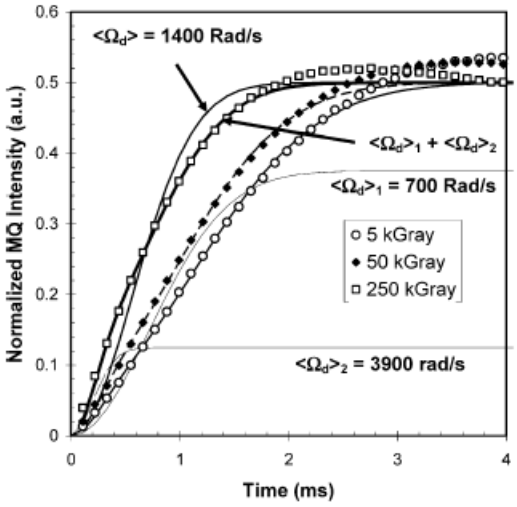


Figure 27. Experimental MQ growth curves for irradiated DC745U samples.

Thermal studies performed using DSC show that the T_g is not affected by cumulative dose while T_m and ΔH_m were observed to decrease with cumulative dose and increased crosslink density.[7] The crystallization temperature decreased with increasing dose due to an increases in crosslink density that stiffens the polymer network and reduces its ability to reorganize.[1,7]

NMR MOUSE experiments were also performed on radiolytic aged DC745U samples and results are consisten with high field NMR experiments, mechanical testings, and solvent swelling experiments.[6,15,17] The general trend is a decrease in the T_2 relaxation time values with increasing radiation dose. The average T_2 values decreased from 107 ms to 93 ms as a function of dose.[6] MRI experiments also show a decrease in T_2 relaxation times with increasing cummulative dose.[6]

LLNL also performed a series of experiments on DC745U samples that were subjected to tensile strain and radiation exposure.[15] The experiments involved permanent set, NMR MOUSE, MQ-NMR, and solvent swelling. The permanent set was observed to be independent of strain but increased with dose reaching to a maximum of 0.50 +/- 0.1 at a radiation dose of 170 kGy. Tensile modulus shows that at a radiation of 170 kGy the materials undergo a dramatic hardening compared to the pristine material, but a moderate softening was seen when the strain was increased, as shown in Figure 28.

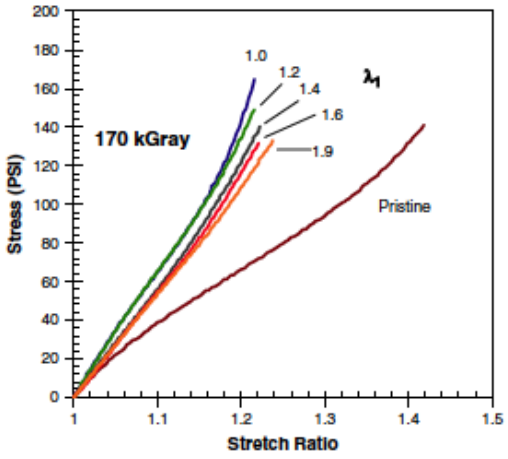


Figure 28. Tensile stress as a function of tensile strain for irradiated samples of DC745 at 170 kGy.

An increased in crosslink density with increasing dose and strain was observed by both NMR MOUSE and MQ-NMR experiments.[15] NMR MOUSE data show a decrease in T_2 relaxation times with increasing dose and strain, while the growth curves obtained by MQ-NMR spectroscopy are faster for the irradiated and strained samples compared to the pristine sample. A faster growth curve means that there is an increased in residual dipolar coupling and crosslink density.

Data obtained from solvent swelling experiments in toluene for the samples aged under radiation show an increase in the crosslink density of the materials of ~140%.[15] However, when the samples where aged under strain the crosslink density did not change. Results obtained from tensile test, NMR MOUSE, MQ-NMR, and solvent swelling indicate that the material's crosslink density is higher after radiation exposure. The tensile test values obtained for the materials under strain a softening of the materials probably due to a reduction in polymer-filler interaction and not a reduction in their crosslink density.

Methods used for the analysis of radiolytically aged DC745U are described in Appendix IV (NMR MOUSE), Appendix V (MRI), Appendix VI (solvent swelling), Appendix XI (tensile tests), Appendix XVI (radiolytic aging), and Appendix XVII (MQ-NMR).

Table 11. Work done on radiolytic aged DC745U by LLNL.

Dose rate	Total dose	Strain	Analytical method
5 kGy/h	0	-	NMR MOUSE, MQ-NMR, solvent swelling, DSC, MRI
	10	-	
	30	-	
	50	-	
	100	-	
	250	-	
	170	1.0	Tensile test, NMR MOUSE, MQ-NMR, solvent swelling
	170	1.2	
	170	1.4	
	170	1.6	
	170	1.9	

4.4 Recommended Further Work

Further thermal aging studies may be needed that include aging for an extended time (> 6 months). Additional radiolytic aging studies should evaluate lower dose rates and total dose. Appropriate pre- and post-aging mechanical testing should be incorporated into new work. New studies should address data needed for system, component and material modeling and validation of those models.

5.0 CONCLUSION

The structure, composition, chemical and physical properties of DC745U have been characterized by a variety of analytical and physical methods. The methods used to study the structure and composition of DC745U were primarily NMR and IR spectroscopy. Based on these techniques, DC745U is made up of dimethyl, methyl-vinyl, and methyl-phenyl siloxane monomers in a ratio of 100:1.0:1.5 and 100:0.2:1 based on LLNL and LANL results, respectively. The presence of silicates used as filler was also confirmed by both NMR and IR spectroscopic techniques.

DC745U pads aged in service have been observed to have deformations. Based on spin echo NMR, MQ-NMR, and solvent swelling experiments these deformations are characterized by areas of lower crosslink density. The deformations are believed to be caused by heterogeneous mixing and molding of the materials.

Spin echo NMR experiments performed on pristine and thermally and radiolytically aged samples suggest that DC745U degrades by a chain-scissioning mechanism when subjected to high temperatures while the same material would undergo a crosslink mechanism when exposed to radiation. The conclusions were based on the fact that the materials will show lower crosslink density when exposed to high temperatures and higher crosslink density when exposed to radiation compared to the pristine material. Results obtained from MQ-NMR, solvent swelling, and mechanical testing are consistent with results obtained from spin echo NMR experiments.

Thermal analysis using DSC and DMA techniques revealed that DC745U has a crystallization temperature of ~ -46°C. The crystallization temperature was observed to increase with crosslink density and radiation cumulative dose.

Tensile test data shows that at room temperature DC745U has an ultimate strain value of 217%. Compressive data show a moderate stiffening of the materials at low temperatures (-40 and -50ºC) and a major change in compressive modulus at -75°C. Similar compressive behaviors are observed for samples at temperatures of -20, 0, and 20ºC for short soak times prior to testing. An irreversible softening is observed with cycling and the damage is amplified at colder temperatures.

6.0 RECOMMENDED FUTURE STUDIES

While a considerable amount of characterization work has been conducted, specific knowledge gaps remain. These gaps should be addressed to improve our understanding of DC745U for systems engineering, surveillance, aging assessments, and lifetime assessment. Specific areas for future work are:

1. Complete characterization of DC745U formulation, including composition of uncured elastomer, peroxide curing agent, and filler. Recommended methods: NMR, IR, TGA, ICP, XPS.
2. Conduct additional low temperature mechanical characterization with focus on soak time, temperature, and thermal cycling. Improve our understanding of low temperature crystallization kinetics.
3. Additional radiolytic and thermal aging studies with appropriate pre- and post-mechanical testings.
4. Develop relationship (or testing methods) between mechanical testing of components and material samples (flat slabs).
5. Detailed review of KCP production process to address milling and post-curing operations, fiberglass mat location, and material acceptance versus part molding conditions.

6. Investigate data used for current models and data needed to improve future models. Pursue strategies to "bridge gap" between system, component and material level models. An example would be, "is there a way to link thermal and radiolytic aging at the material level to modeling (and lifetime prediction) of the component in the actual system?" Implement strategies for model validation.
7. Develop a complete and complementary suite of NMR tools such as spin-echo NMR, MRI, and CPMAS-NMR. NMR tools can be developed in collaboration with LLNL (with feedback from production agencies) such that materials can be tested and screened efficiently and accurate data reproduced and compared at both labs.

7.0 REFERENCES

(1) Maxwell, R. S.; Chinn, S. C.; Herberg, J.; Harvey, C.; Alviso, C.; Vance, A.; Cohenour, R.; Wilson, M.; Solyom, D. *Baseline and Lifetime Assessments for DC745U Elastomeric Components*, Lawrence Livermore National Laboratory, 2005.

(2) Iuliucci, R.; Taylor, C.; Hollis, W. K. *Magn. Reson. Chem.* **2006**, *44*, 375.

(3) Labouriau, A. *DC745*, Los Alamos National Laboratory, 2011.

(4) *Plan Information: Pressure Pads*, Kansas City Plant.

(5) Sanders, R. S. *Compressive Stress Relaxation of Candidates for B-61 Ribbed Pressure Pad*, Kansas City Plant, 1981.

(6) Herberg, J. L.; Chinn, S. C.; Savel, A. M.; Gjersing, E.; Maxwell, R. S. *Polym. Degrad. Stab.* **2006**, *91*, 1701.

(7) Maxwell, R. S.; Chinn, S. C.; Solyom, D.; Cohenour, R. *Macromolecules* **2005**, *38*, 7026.

(8) *Test Report: Dow Corning 745U*, DatapointLabs, 2002.

(9) JWS *Density Determination of DC-745 Material at KCP*, 2010.

(10) DatapointLabs; http://www.datapointlabs.com/TestDetails.asp?TestId=3.

(11) Coons, J.; Rutherford, S. *Oxygen Depletion from DC745 and Evaporation Rates of Water Droplets*, Los Alamos National Laboratory, June 15, 2001.

(12) Labouriau, A. *DC745*, Los Alamos National Laboratory, 2011.

(13) Dattelbaum, D.; Orler, E. B.; Rae, P.; Brown, E.; Cady, C.; Tornga, S.; Sheffield, S.; Shaw, S.; Clements, B.; Patterson, B.; Laboriau, A.; Welch, C.; Kober, E.; Lewis, M.; Peery, T. *Dynamic Response of Weapons Polymers*, Los Alamos National Laboratory, 2010.

(14) Orler, E. B.; Tornga, S. C. *Preliminary Data on the Thermal Properties od DC745U*, Los Alamos National Laboratory, 2010.

(15) Chinn, S.; DeTeres, S.; Sawvel, A.; Shields, A.; Balazs, B.; Maxwell, R. S. *Polym. Degrad. Stab.* **2006**, *91*, 555.

(16) Cady, C. M.; Dattlebaum, D.; Lillard, J.; Liu, C.; Laboriau, A. *Mechanical Characterization of DC745 and Fogbank*, Los Alamos National Laboratory.

(17) Chinn, S. C.; Herberg, J. L.; Sawvel, A. M.; Maxwell, R. S. *Mater. Res. Soc. Symp. Proc.* **2005**, *851*, NN11.6.1.

(18) Labouriau, A.; Stephens, T. S. *Report on Assessment of Aging in Polymers*, Los Alamos National Laboratory, 2008.

(19) Stephens, T.; Labouriau, A. *Solid-State NMR Studies for DC745: April-May 2000*, Los Alamos National Laboratory, 2000.

APPENDIX A

I. Solid State NMR (LLNL)

The instrument used is a 9.4T Bruker Avance 400 operating at a frequency of 400.10 MHz. Multiple Quantum (MQ) NMR were performed using the refocused multiple quantum excitation and reconversion pulse described by Saalwachter (*J. Chem. Phys*. 120, 454 (2004)).

II. ^{1}H-NMR Measurements (LLNL)

Measurements were performed at 400.13 MHz on a Bruker Avance 400 spectrometer using a Bruker TBI (HCX) 5 mm probe. ^{1}H $\pi/2$ excitation pulses of 6 μs and relaxation delays of 7 s were used. In all cases, small (0.1 cm x 0.1 cm x 0.1 cm) squares of elastomers were cut from a larger piece and set in the portion of a 5 mm NMR tube that would be within the coil volume of the probe.

III. NMR Studies by Washington and Jefferson College[2]

NMR experiments were performed on a Varian Inova spectrometer with a wide bore 9.4 Tesla Oxford magnet. The operational frequencies were 399.80 MHz and 79.426 MHz for ^{1}H and ^{29}Si, respectively. All spectra were acquired at room temperature and referenced externally to liquid TMS. Varian Chemagnetics T_3 double resonance probes, 4.0 mm and 7.5 mm, were used. Magic angle spinning with an automated spin controller was employed at a speed between 2.0 and 5.0 kHz for ^{29}Si spectra. The ^{1}H spectrum was acquired at 15 kHz, spinning with the high-speed-spinning-assisted WaHuHa pulse sequence. A 90° pulse width of 4.0 and 5.5 μs for ^{1}H and ^{29}Si was employed respectively. For the ^{29}Si spectra, relaxation delays of 2-120 s were used. The signal was detected under 27 kHz of continuous wave decoupling, 0.05 ms acquisition time, and a dwell time that produced a 250 ppm spectral window. For cp

experiments, the duration of the Hartmann-Hahn match was arrayed from 0.1-20 ms for variable $^{1}H/^{29}Si$ contact time data. A spin-lock field of 47 kHz was used during the Hartmann-Hahn match condition. The 2D HetCor experiments incorporated frequency-switched Lee-Goldburg homonuclear decoupling during the f_1 period. A mixing time of 10 ms was used during cp in the 2D HetCor experiment. The peak intensities from variable contact-time data were analyzed in a curve-fitting tool of Matlab.

IV. NMR MOUSE experiments performed by LLNL[6]

Samples were 1 cm x 1 cm pieces and were placed in the center of the surface coil. The experiments were performed on a NMR MOUSE (Mobile Universal Surface Explorer) from Bruker Optics operating at 16 MHz. The experimental parameters were set as follow: echo time of 0.25 ms with 1500 echoes time per experiment and 512 scans signal averaged per echo time. The echo times were systematically increased until the T_2 remained consistent to avoid interfering effects of T_{1p} in ghd CPMG experiment. The pulse attenuation, receiver gain, and recycle delay were set to 6 dB, 103 dB, and 1 s, respectively. Decay curves were fit to a two-component exponential decay using the Bruker software. Further data processing was performed with the Contin application from Bruker Optics, which uses and inverse Laplace transform to yield the distribution of T_2 relaxation times.

V. MRI experiments performed by LLNL[6]

All MRI experiments were performed on a Bruker Avance 400 MHz spectrometer equipped with a high-resolution Micro5 microimaging system with either a 25 mm RF coil or a 5 mm RF coil depending on the size of the sample. The resulting images had a Field-of-View (FOV) of 3.0 by 3.0 cm with a resolution of 0.234 mm/pixel by 0.234 mm/pixel. The excitation pulse length was 10 ms, the detection time was 204.16 ms,

two averages were obtained, and the total experiment time was 8 min and 13 s. The slice thickness was 1 mm. For these experiments the FOV was 6.0 cm by 6.0 cm with a resolution of 0.234 mm/pixel by 0.234 mm/pixel. The slice thickness was 2 mm. The 2D T_2 weighted MRI experiment was carried out with an echo time of 10.25 ms, a repetition time of 1 s, one average, and a total time of 4 min and 16 s. For the samples exposed to γ –radiation, 2D T_2 weighted NMR experiments were performed with a Field-of-View (FOV) of 2.15 cm by 2.15 cm with a resolution of 0.168 mm/pixel by 0.168 mm/pixel. The slice thickness was 2 mm. The 2D T_2 weighted MRI experiment was carried out with an echo time of 8 ms, a repetition time of 1 s, four averages, and a total time of 8 min and 34 s.

VI. Solvent Swelling Experiment performed by LLNL[7]

The samples were weighted (1g) for the initial weight and then submerge in 600 mL of toluene in a sealed Teflon container while stirring. The swollen weight of the samples was measured until an equilibrium weight was obtained (3 days). Then, 150 mL of 28 wt% of ammonia was added directly to the toluene solution, the container was resealed, and stirring continued. The samples were weighted periodically until the equilibrium was reached with the ammonia/toluene mixture (30 days). The samples were then dried overnight under vacuum, or under ambient conditions for 7 days and reweighted for the final dry weight. The weights were then used in a modified Flory-Higgins approach discussed in detail in ref… to obtain the crosslink density due to the polymer network, the polymer, and the filler.

VII. DSC Experiments performed by LLNL[7]

DSC analyses were performed on a TA Instruments, MDSC Q1000 by cooling the sample at a rate of 1.50 ºC/min to -160 ºC from room temperature. Subsequent heating of the samples was then performed at

1.50 ºC/min with a modulation frequency of ± 0.16 ºC/40s.

VIII. Bulk Density Determination at DatapointsLab[10]

A container of a precisely known volume is filled with sample pellets. These pellets are then removed and weighed using an analytical balance. This procedure is repeated three times. The bulk density is calculated from the volume and mass, and the average of the three tests is reported.

IX. Density Determination at Kansas City Plant[9]

The density was determined by weight and volume displacement. The weight of a 1 square inch sample weighted 2.7112 g and the volume was 2.0 cc. The resulting density was 1.355 g/cc.

X. Tensile Properties Measurements performed by Datapoint Labs[8]

The instrument used as an Instron 5566 Materials Testing System with a method based on ASTM D 412-98a. The parameter used were the following: test temperature= 24 ºC, 71 ºC, and 54 ºC, lab humidity= 0 and 52 %RH, crosshead speed= 500 mm/min, and number of replicates= 5. The video field of view was 350 mm and 50 mm, and the extensometer class as B-1 at GL= 175 mm. The samples were type C dumbbells with dimensions of 6.4 mm x 2.0 mm x 25 mm (width x thickness x length).

XI. Tensile Tests Performed by LLNL[15]

Tensile tests were performed on virgin and irradiated specimens. All testing were performed with an electromechanical test system (MTS Synergie 1000 lb) equipped with pneumatic grips and a 50 N load cell. The change in width of specimens was measured during tensile testing using a laser micrometer (Keyence LS-5041). The micrometer was mounted on a movable frame to allow the specimen width to be measured at a fixed location along the specimen length during the test. Initial lateral dimentsions of the tensile speciments were determined

using a comparator, Nikon Profile Projector V-12, to measure width and a height gauge to measure thickness. Specimens were tested using an initial gauge length of 1.25 in. and a displacement rate of 0.2 in./min.

XII. Compressive Tests Performed by Datapoint Labs[8]

The instrument used was an Instron 5566 Materials Testing System with a method based on D 575-91 (2001). The parameter used were the following: test temperature= 23 °C, 71 °C, and -54 °C, crosshead speed= 13 mm/min, and number of replicates= 3, 4, and 6. The samples had dimensions of 32.1 mm x 12.7 mm (diameter x thickness).

XIII. Compressive Tests Performed by LANL

The instrument used was an MTS 880 load frame with a test star IIm controller. The tests shown in this report were held at the test temperature to reach an equilibrium temperature before testing (~ 5 minutes). A variable loading rate that simulated a "true strain rate" was calculated based on the initial sample dimensions and a test profile was generated based from these calculations. Tests conducted below room temperature were conducted by cooling the load stage with liquid nitrogen expanding from a dewar in a gaseous state and flowing through channels designed in the loading platens. Controlling the flow rate is the mechanism by which temperature is controlled.

XIV. PVT method by Datapoint Labs

The pressure-specific volume-temperature measurements were performed using a high-pressure dilatometry. The specimen was dried at 70 °C under vacuum for 4 hours. The parameters were the following: solid density method was ASTM D792, immersion liquid= water, pvT confining liquid= mercury, maximum temperature= 255 °C, measurement type= isothermal heating, and the heating rate= 3 °C/min.

XV. Aging Conditions by LANL[18]

The samples were accelerated aged under compression atmosphere and at different temperatures for 6 months. Samples remained in their fixtures and in seal cans for up to 6.5 yeas. The temperatures used during the aging process were 80 °C and 120 °C, and other conditions involved dry or wet environment, excess of oxygen, and irradiation. After compression the samples were kept in their fixture for a total of 6.5 years before analyzing them. Some samples were post-cured at 140 °C for 40 min and 239 °C for 8 hours, some other samples were not post-cured at all.

XVI. Radiolytic Aging by LLNL[1,6,7,15,17]

The samples were exposed to a ^{60}Co source (1.2 MeV) at 5 kGy/h for times necessary to expose the samples to 5 - 250 kGy. Some samples were subjected to tensile strain during radiation exposure.

XVII. MQ-NMR by LLNL

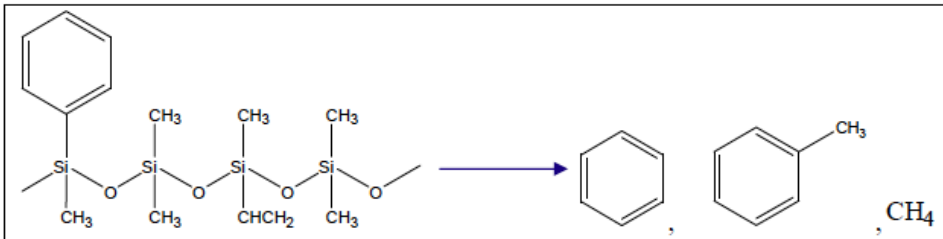
Described elsewhere.[7]

XVIII. Solid Phase Micro Extraction (SPME) GC/MS

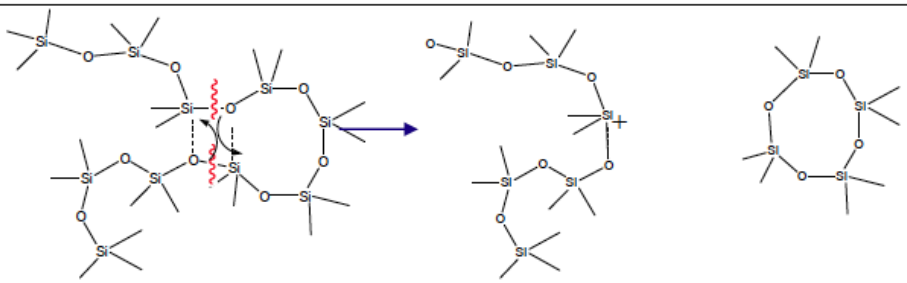
Carboxen/PDMS (85 μm) SPME fibers were purchased from Supelco. SPME headspace vials (20 mL), crimp caps and septa (20 mm, teflon/blue silicone, level 4) werepurchased from MicroLiter Analytical

Supplies. Three samples, weighing approximately20-30 mg each, were placed in 20 mL SPME headspace vials. One set of Sylgard 184 samples (pristine and irradiated) were analyzed as-is and one set was placed in a 70°C oven for two weeks. Headspace SPME analyses for a given radiation dose and temperature were performed on a blank control vial and Sylgard 184. The samples were analyzed by SPME GC/MS using an automated system under the following conditions: 85 µm Carboxen/PDMS SPME fiber, conditioned between samples for five minutes at 260˚C; headspace sampled at 50˚C for 20 minutes and injected into the GC for one minute at 250˚C. The Agilent 6890 GC was set for splitless injection and purged at 0.5 minutes using a J & W Scientific DB-624 column (30 m, 0.25 mm ID, 1.4 µm film) with a 1.0 mL/min constant flow of helium. The 20-minute run had the following temperature profile: 40˚C/1.05 min., 23.41˚C/min. to 260˚C, and held 6.81 min. An Agilent 5973 mass spectrometer scanned the mass range from 35-450 at a rate of 1.81 scans/s with no filament delay. Outgassing products were identified by comparison of their mass spectra o the NIST 02 mass spectral library.

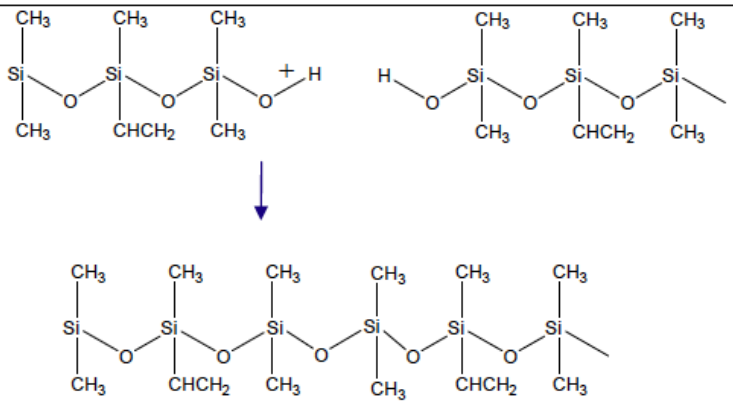
XIX. Degradation Mechanisms of Silicone Elastomers (picture taken from Robert Maxwell report *Baseline and Lifetime Assessments for DC745U Elastomeric Components*)



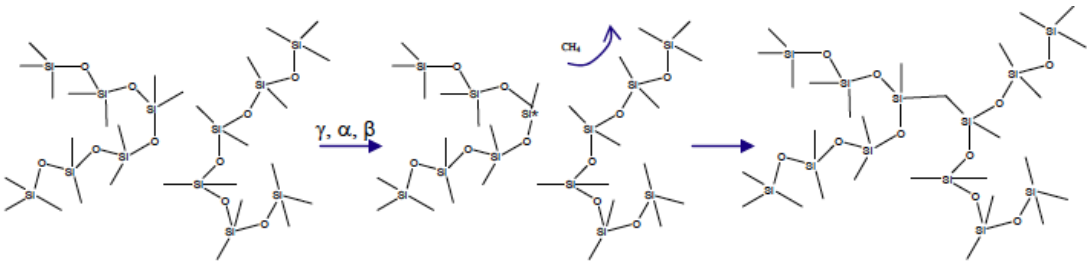
Fragmentation reactions



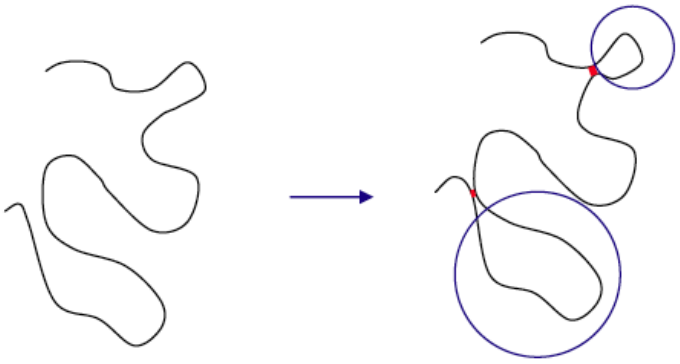
Backbiting/chain scission reactions



Condensation reactions



Radiation induced Crosslinking of two chains



Production of elastically ineffective segments (crosslinks shown in red, ineffective segments circled in blue).