LA-UR-13-25885
Approved for public release; distribution is unlimited.

Title:	Low Temperature Studies on DC745U Pressure Pads
Author(s):	Ortiz-Acosta, Denisse
Intended for:	Report
Issued:	2013-07-26

Low Temperature Studies on DC745U Pressure Pads

Denisse Ortiz-Acosta (C-CDE)
Principal Investigator

Team:
Michael Janicke (C-IIAC)
Carl Cady (MST-8)
Bruce Orler (formerly MST-7)

Los Alamos National Laboratory, Los Alamos NM 87545

TABLE OF CONTENTS

Mission Statement

As part of the Enhanced Surveillance mission, the goal is to provide suitable lifetime assessment of non-nuclear materials. This report is an accumulation of experimental data to fully understand the low temperature behavior of DC745U- pressure pad. The intention is that the B61 Life Extension Program (LEP) use this collection of data to further develop their understanding and potential areas of study.

Acknowledgments

Tom Zocco, C8 Program Manager
Dana Dattelbaum, C2 Project Leader
Steve De La Torre, B61 Weapon System Engineer
Jennifer Gallegos, Project Leader

1.0 INTRODUCTION

DC745U is a silica-filled solid silicone elastomer used to manufacture pressure pads for a variety of applications. The material is proprietary to Dow Corning and thus very little information on its composition and properties is available. A considerable amount of characterization work has been conducted (*Denisse Ortiz-Acosta W-1-TR-0098U/ LA-UR-12-23612*) on DC745U. Based on these studies an estimate of the composition of the polymer was obtained. DC745U is composed of ≤ 100 wt% dimethyl siloxane repeat units, ≤1.5 wt% of methylphenyl siloxane, and ≤ 1 wt% methylvinyl siloxane groups. The methylvinyl siloxane groups are used as crosslink sites. The polymer is cured using a vinyl-specific peroxide, Varox DBPH-50, at 160ºC to form a polymer network. The structure and composition of this polymer network provide DC745U its unique properties.

The methylphenyl siloxane repeat unit was added to improve DC745U's thermal properties when compared to polydimethylsiloxane (PDMS). PDMS has a glass transition temperature of -120ºC and a melting temperature of -40ºC. It is believed that the phenyl group in DC745U improves thermal properties by inhibiting crystallization. This report describes the results obtained from low temperature thermal, mechanical and molecular characterization. These studies were conducted to improve our understanding of low temperature crystallization kinetics and thermal kinetics under compression strain and to determine if the pad undergoes stress deformations under these extreme conditions. Results described herein address several knowledge gaps previously stated in the report *W-1-TR-0098U*. Experiments described here include Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA), Nuclear Magnetic Resonance (NMR), and mechanical (stress/strain) tests.

2.0 EXPERIMENTAL INFORMATION

2.1 Differential Scanning Calorimetry

The thermal measurements were performed on a TA Instrument Q2000 Modulated Differential Scanning Calorimeter (MDSC) with a liquid nitrogen cooling accessory with helium purge. The sample was rapidly cooled to -20ºC, and then cooled at 2ºC/min to -150ºC. The sample was equilibrated at -150ºC and then heated at a rate of 10ºC/min to 100ºC. The T_g was defined as the midpoint height of the step transition and the heats of crystallization and melting were determined by integrating the endothermic and exothermic peaks from -100ºC to ~ -40ºC.

2.2 Dynamic Mechanical Analysis

The dynamic mechanical properties were determined using an Ares Rheometer (TA Instrument, Inc.) under torsional deformation. The samples were cooled using a liquid nitrogen cooling accessory and heated at a rate of 2ºC/min.

2.3 Nuclear Magnetic Resonance

CPMG T_2 variable temperature measurements were done on a Bruker Biospin 300 MHz NMR liquids spectrometer with variable temperature capabilities from 150^{o}C to -150^{o}C. T_2 is a measure of the rate at which transverse magnetization is lost in the x-y plane during a NMR experiment as the spins return to equilibrium along the z axis. It is a direct

measure of the motional diffusion rates of the polymer and hence the degree of cross linking. Keep in mind the T_2 is inversely correlated to the viscosity, short T_2's are observed for rigid, crystalline states and long T_2's are found in liquids and plastic phases. The pulse sequence was the standard CPMG sequence with 8.23 μsec π/2 and 16.46 μsec π pulses for ^{1}H. A 200 μsec delay was used before and after the π pulses. The probe was tuned at each temperature and different sample to ensure reliable pulse lengths and power levels. A 6.5 s recycle delay was used between acquisitions for full T_1 relaxation; T_1 was measured to be approximately 1.2 s for ^{1}H in this material. Samples were not spun and cooling was achieved under dry nitrogen gas. Samples were held at final temperatures (25°C, -50°C, and -70°C) for 5 min to ensure temperature equilibrium.

2.4 Stress/Strain Analysis

Mechanical tests were conducted on an MTS model 880 using constant strain rate loading with a liquid nitrogen cooled cold stage. The cold stage cools the specimens by controlling the volume of gas passing through the loading platens and temperatures were maintained to within ± 1°C. The load signal was captured on the 10 kN range of the system load cell and with a 500 lb cell as a second load cell for tests conducted at loads that would not reach 2 kN maximum load. Displacement was measured between the metallic platens using a crack opening displacement gage calibrated in the compressive direction. Displacements were also recorded from the system LVDT but this data was not used during analysis of the Stress and Strain. The analysis of the data was done with the assumption of incompressibility and the True Stress and True Strain was calculated using sample dimensions and traditional equations for both strain and stress. Test temperatures where held for at least five to ten minutes before testing to reach thermal equilibrium. Longer dwell times were used for some temperatures to determine the material behavior near the crystalline phase transition.

3.0 RESULTS AND DISCUSSION

3.1 Differential Scanning Calorimetry

For DSC analysis the samples were cooled rapidly to -100ºC and then to -150ºC at a rate of 2ºC/min. The samples were then warmed to room temperature at a rate of 10ºC/min. Results are shown in Figure 1 and indicate that DC745U has a glass transition temperature (T_g) of ~ -122ºC, similar to that of PDMS. The glass transition temperature is the temperature at which the material becomes brittle. An endothermic peak is observed between -80ºC and -40ºC associated to the melting of crystallites. The heat of fusion is 14 J/g. Upon cooling the melt at a rate of 5ºC/min a crystallization temperature of -61ºC is observed. The crystallization temperature is the temperature at which small crystalline domains within the polymer forms and the polymer becomes stiffer. It is between the T_g and crystallization temperature where significant changes in mechanical properties occur as it is observed from experiments below.

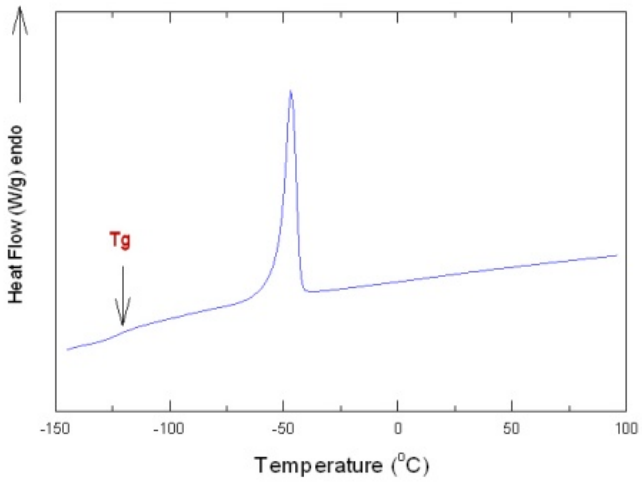

Figure 1. DSC analysis of DC745U.

3.2 Dynamic Mechanical Analysis

DMA results show that DC745U initial shear modulus (G') at room temperature is 3 MPa. Upon cooling there is a slight increase in G' up to a temperature of -60ºC. The G' increases by 2 orders of magnitude at temperatures between -60 and -80ºC due to the formation of crystalline domains within the polymer. At temperatures between -100 and -133ºC another slight increase in modulus is observed and is associated with the glass transition temperature. Upon heating, the G' curve traces the cooling curve up to -100ºC. The G' remains higher until the sample reaches -40ºC after which the heating curve traces the cooling curve. A drastic change in modulus is observed at temperatures between -52ºC and -40ºC and is the result of the melting of the crystalline domains formed during cooling conditions. Figure 2 represent the dynamic mechanical properties of DC745U.

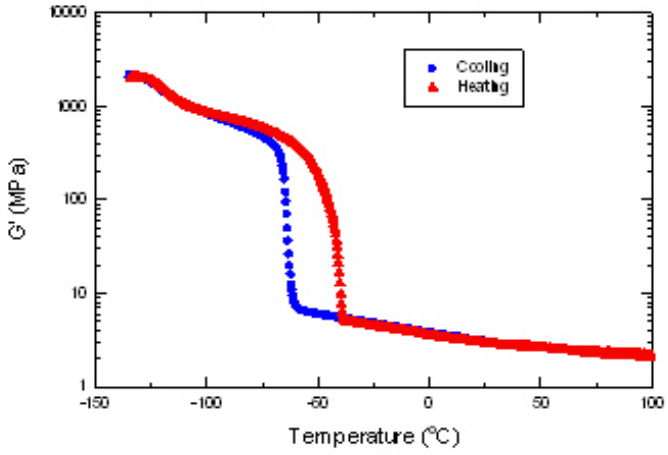

Figure 2. Shear storage modulus (G') of DC745U at a temperature range of -150ºC to 100ºC.

Isothermal DMA measurements were conducted on DC745U to understand the rate of crystallization and changes in modulus (G') at low temperatures. The experiments were performed at -48, -50, -52, -54, -57, -60, and -65 ºC and the time it took the polymer to crystallize was recorded. Results are represented in Figure 3 and show that crystallization has a significant effect on the bulk modulus of the polymer. The G' increases by two-orders of magnitude after the crystalline transition has occurred. It is observed that crystallization is not an instantaneous process but a kinetically-driven process. At temperatures of -48 and -50ºC, it takes over 240 minutes (>4 hours) for the crystalline transition to take place. The transition occurs faster at lower temperatures. At -52ºC it takes ~ 2 hours for the transition to take place. At temperatures below -54ºC the transition occurs in less than 60 minutes. For all isothermal experiments the modulus plateaus at G'≈ 1000 MPa. It can be expected no significant changes in mechanical properties will be observed between crystallization and T_g of DC745U.

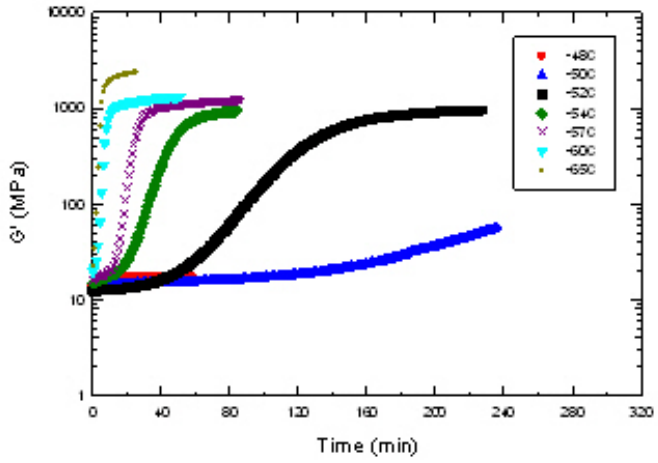

Figure 3. Low Temperature isothermal DMA on DC745U.

3.3 Nuclear Magnetic Resonance

Spin echo NMR experiments at low temperatures were performed to observe the crystalline phase transition and if there is permanent damage induced with excursion to low temperatures. This technique looked specifically at the molecular dynamics of DC745U by studying the mobility of the polymer chains, short T_2's are observed for rigid, crystalline states or polymers with high crosslink density and long T_2's are found in mobile polymers or polymers with lower crosslink density. The relaxation time of the sample was initially determined at 25ºC. The sample was then cooled to -50ºC, held for 5 minutes to ensure temperature equilibrium, and T_2 was determined. The sample was cooled further to -70ºC, held for 5 minutes, and T_2 was determined. Finally, the sample was warmed up to room temperature and the T_2 was determined at time= 5, 18, and 30 minutes to identify time needed for the material to recover to its original state.

The data obtained at the different temperatures for DC745U is summarized in Figure 4 and Figure 5. The initial experiment at room temperature shows the material's viscoelastic behavior and a T_2= 20.50 ms. The T_2 experiment measured at -50ºC show a

faster decay that is attributed to stiffening of the polymer. The drastic change in relaxation time from T_2= 20.50 ms to T_2= 3.37 ms describes the crystalline phase transition that the material undergoes at -50ºC. This observation correlates well with DMA experiments and mechanical test results (below). The experiment was repeated at -70ºC below crystalline transition temperature. At this temperature the T_2= 0.67 ms is very short indicating further stiffening of the polymer and complete crystallization. Finally, the sample was returned to room temperature and multiple data sets were collected at t= 5, 18, and 30 minutes. The data in Figure 4 and 5 show that DC745U chemical properties mostly recover to their original T_2 (18.84, 19.21 and 19.80, respectively) value. It seems that there is a small but not significant change in T_2 relaxation time. It does not appear that the material undergoes any permanent damage at this temperature range.

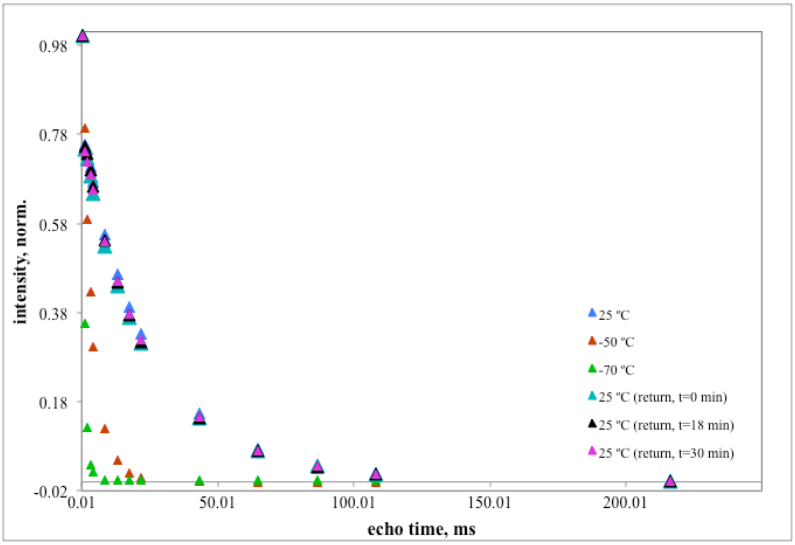

Figure 4. Exponential decay data summary for DC745U.

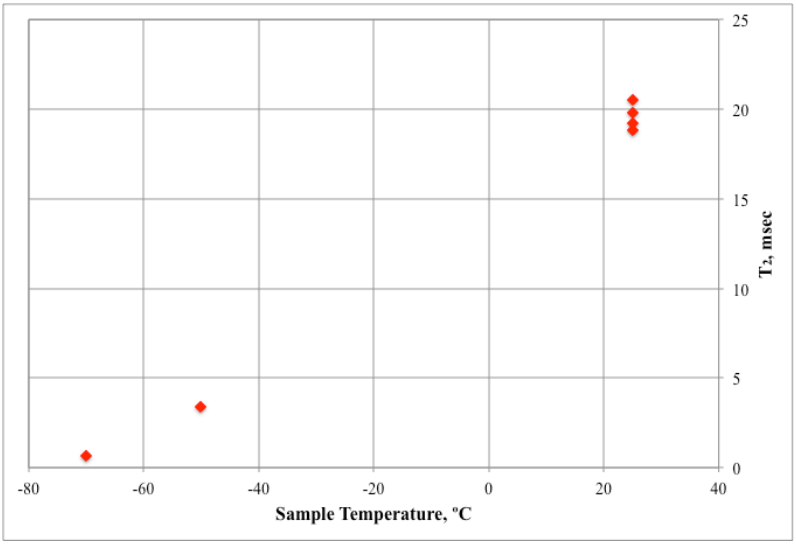

Figure 5. Summary of T_2 values versus temperature from single exponential decay.

3.4 Stress/Strain Mechanical Tests

Compressive tests were performed on DC745U as a function of temperature and strain rates from -55ºC to 75ºC and from 0.001/s to 1/s, respectively. Figure 6 shows the stress-strain behavior on DC745U as a function of temperature at a strain rate of 0.01/s. The data shows stiffening of DC745U at temperatures below -50ºC. This stiffening is a result of a crystalline phase transition. Cyclic loading of all test samples was done to determine if the material undergoes typical Mullins behavior and deformation. Samples were held at the desired temperature for 1 hour prior to beginning the loading cycles (Fig. 6). The samples were then cycled three times to 50% engineer strain and unloaded. Once the first set of load cycles was completed the material was allowed to warm to 20ºC and left for an hour before additional load cycles to 50% strain were applied. Finally, the samples were cooled again to the desired temperature, held for 1 hour and reloaded for an additional three cycles to 50% strain. The same cyclic loading experiments were performed starting with three cycles at room temperature, then three cycles at the desired cold temperature, and finally three cycles at room temperature. In the plots below (Fig. 6) the loading segments are offset by 10% and 20% for clarity. At temperatures above -50ºC there appears to be a slight differences between the first cycle and subsequent loading cycles indicating that the material undergo some changes during the first cycle. This is due to Mullins effects occurring during the first loading cycle. There also appears to be a slight change in the materials behavior after the first cycle at room temperature but is less pronounced. There is no evidence of recovery for the reloading at low temperatures. Similar Mullins effect is observed for DC745U samples during cyclic loading that began at room temperature, followed by low temperature, and finally room temperature. For test conditions at temperatures above -50ºC DC745U retains its viscoelastic properties and the loading modulus of the material does not appear to change during the loading event. In addition, the material does not show any permanent or retained deformation for these test conditions.

At temperatures $\leq$ -50ºC there is evidence of a crystalline phase transition after the first cycle. As long as the material is kept at low temperature there is no evidence of recovery. The material seems to fully recover after it is warmed up to room temperature. The phase transition is also observed during reloading at low temperature and occurs faster at lower temperatures. This result agrees with DMA observations and indicates that crystallinity is a kinetically driven process. When the samples were initially loaded at room temperature a small Mullins effect was also observed and retained through subsequent load cycles. For test conditions at temperatures $\leq$ -50ºC DC745U does not undergo permanent deformation and recovers its viscoelastic behavior at warmer temperatures.

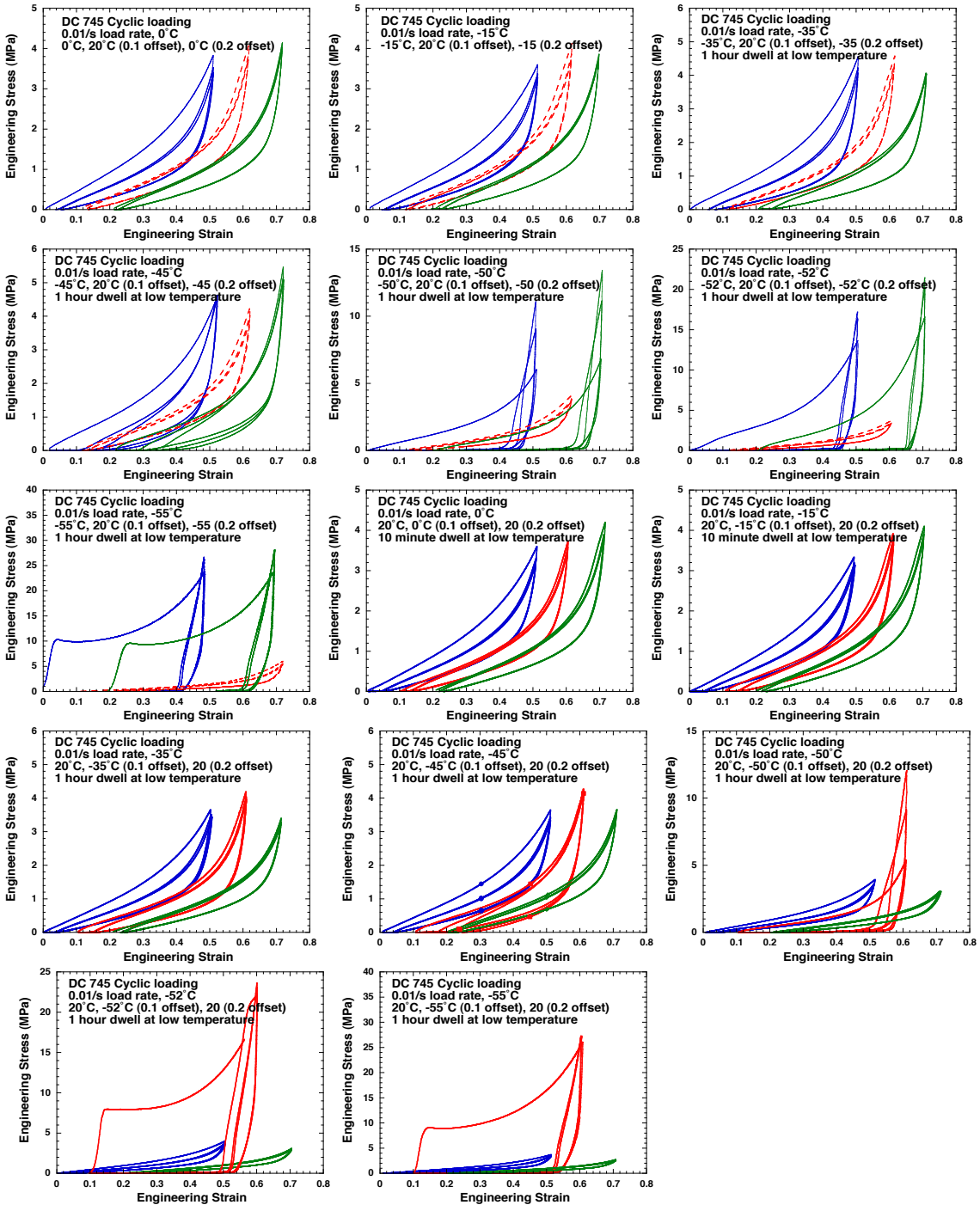

Figure 6. Cyclic loading data on DC745U as a function of temperature and a 0.01/s strain rate.

Figure 7 represents data collected at a constant temperature for the three strain rates investigated (1.0/s, 0.01/s, and 0.001/s). The results show that there is little or no temperature and/or strain rate effect in DC745U at temperatures ≥ -45ºC. At temperatures ≤ -50ºC there is an indication of increasing loading modulus or stiffness as the strain rate

decreases from 1.0/s to 0.001/s. This result is an indication that the crystalline phase transition is a kinetically-driven process. At slower strain rates the material has been at temperature for longer times allowing sufficient time for crystallization. At -50ºC the transition becomes evident at a 0.001/s strain rate; and at -55ºC the onset of crystallinity shows at strain rates of 0.01/s and slower. For these tests a new sample was used for each change in strain rate or temperature. For each test conditions the sample was allowed to equilibrate at the test temperature for at least 10 minutes before the load was applied.

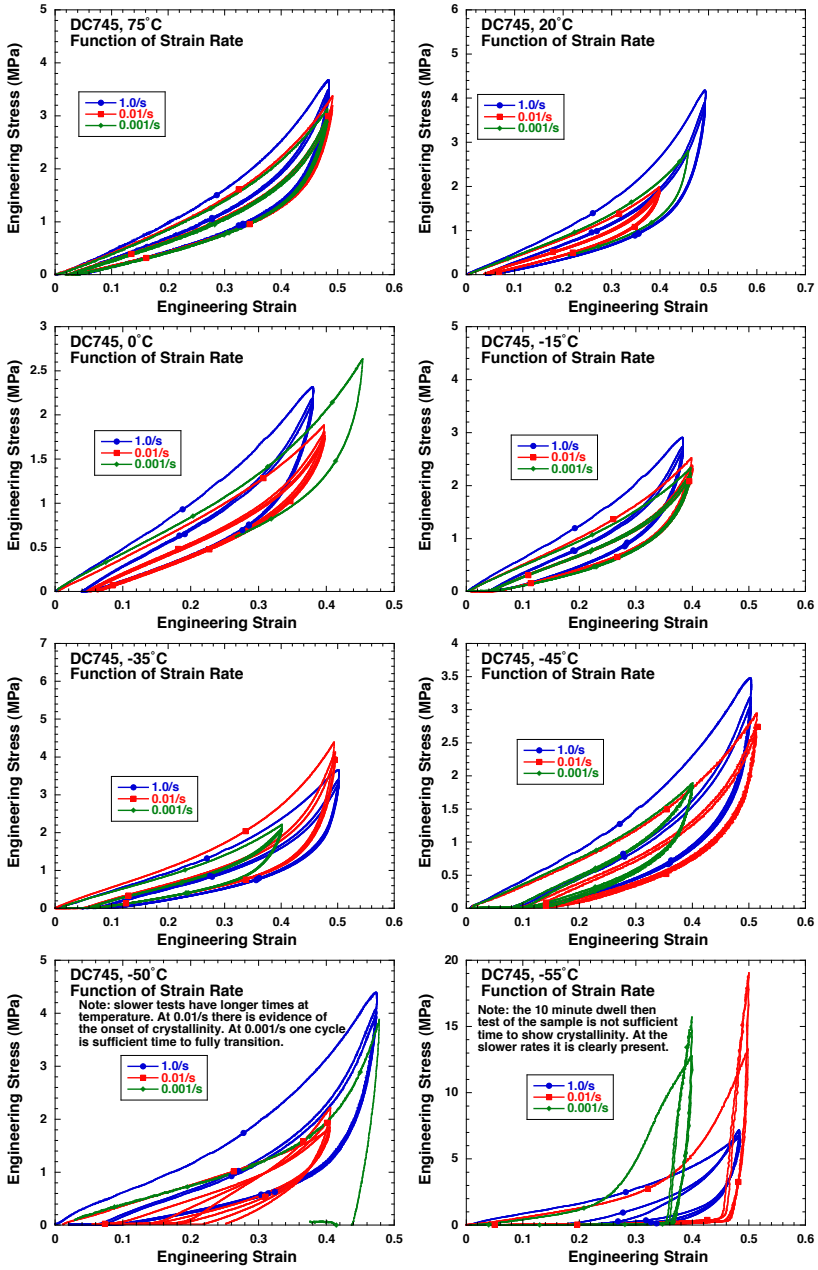

Figure 7. Load test performed on DC745U as a function of strain rate.

In Figure 8 (the blue line represents the stress and the red symbols represent temperature) the material was loaded at a 0.01/s strain rate to ~ 50% engineering strain. At 50% strain

the sample was cooled to -55ºC and held at temperature for 1 hour and finally allowed to warm to room temperature. The blue and red curves represent the temperature and stress, respectively, as a function of time. The results show that the stress of the sample drops rapidly to near transition with decreasing temperature and remains constant for as long as the temperature is held at -55ºC. DC745U recovers quickly when it reaches temperatures above -40ºC. The material seems to fully recover to its initial viscoelastic properties and no significant changes in modulus and/or Mullins effect are observed.

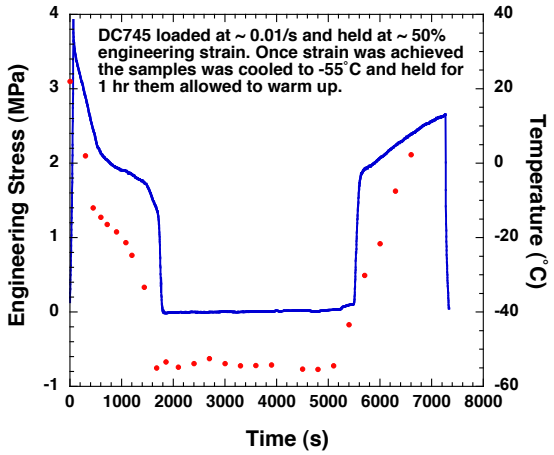

Figure 8. Compressive displacement of DC745U as a function of time and temperature. (The blue line represents the stress and the red symbols represent temperature)

4.0 CONCLUSIONS

The low temperature behavior of DC745U was studied using a variety of analytical techniques. Low temperature behavior of this pressure pad material was a specific knowledge gap addressed in a previous report, "Historical Material Analysis of DC745U Pressure Pads" (*Denisse Ortiz-Acosta W-1-TR-0098U/ LA-UR-12-23612).* The methods used for this study were DSC, DMA, NMR, and mechanical testing. Experiments show the following results:

1. DSC results indicate that the material has a T_g= -122ºC, T_c= -61–C, and T_m= -40ºC.

2. DMA shows that crystallization occurs at temperatures between -80ºC and -60ºC, and the glass transition temperature occurs at temperatures between -100ºC and -133ºC. DMA also shows a T_m= -40ºC.

3. Isothermal DMA shows that the formation of crystalline domains is a kinetically driven process. Crystallization kinetics increase at lower temperatures.

4. NMR spectroscopy shows that crystallization causes a decrease in relaxation time T_2 due to stiffening of the polymer. The material's chemical properties recover upon increasing temperature to ambient conditions.

5. Mechanical tests show a phase transition at temperatures ≤-50ºC when the material is under applied load (50% strain) due to the formation of crystalline domains. Under applied strain, the material recovers its viscoelastic properties when it reaches -40ºC.

6. Mechanical tests show that the formation of crystalline domains is a kinetically driven process.

From these results it can be concluded that DC745U pressure pad has a T_g= -122ºC, T_c= -60ºC, and a T_m= -40ºC at which the material completely recovers its viscoelastic properties. Under applied load the crystallization temperature increases to -50ºC and the T_m remains -40ºC. DC745U does not seem to undergo any permanent damage at temperatures between -122ºC and -50ºC.