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# Crystallization Behavior of Virgin TR-55 Silicone Rubber Measured Using Dynamic Mechanical Thermal Analysis with Liquid Nitrogen Cooling

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## SUMMARY

Dynamic mechanical thermal analysis (DMTA) of virgin TR-55 silicone rubber specimens was conducted. Two dynamic temperature sweep tests, 25 to -100°C and 25 to -70 to 0°C (ramp rate = 1°C/min), were conducted at a frequency of 6.28 rad/s (1 Hz) using a torsion rectangular test geometry. A strain of 0.1% was used, which was near the upper limit of the linear viscoelastic region of the material based on an initial dynamic strain sweep test. Storage ( $G'$ ) and loss ( $G''$ ) moduli, the ratio  $G''/G'$  ( $\tan \delta$ ), and the coefficient of linear thermal expansion ( $\alpha$ ) were determined as a function of temperature. Crystallization occurred between -40 and -60°C, with  $G'$  increasing from  $\sim 6 \times 10^6$  to  $\sim 4 \times 10^8$  Pa. The value of  $\alpha$  was fairly constant before ( $\sim 4 \times 10^{-4}$  mm/mm-°C) and after ( $\sim 3 \times 10^{-4}$  mm/mm-°C) the transition, and peaked during the transition ( $\sim 3 \times 10^{-3}$  mm/mm-°C). Melting occurred around -30°C upon heating.

## MATERIALS AND METHODS

The Dow Corning TR-55 silicone rubber material was made at Kansas City Plant. Specimens were cut by hand from a sheet using a scalpel. Specimens were approximately 45 mm long  $\times$  12 mm wide  $\times$  2 mm thick. Dynamic mechanical thermal analysis (DMTA) was conducted using the TA Instruments ARES rheometer with liquid nitrogen cooling in B132S R2729; the instrument was controlled by TA Orchestrator software. A torsion rectangle test geometry was used. The auto-tension feature was used to maintain a tensile force of approximately 10 g during the test by automatically adjusting the gap distance to compensate for thermal expansion/contraction of the specimen. Dynamic temperature ramps were recorded for the following two temperature profiles: (1) cool from 25 to -100°C at a rate of 1°C/min and (2) cool from 25 to -70°C at a rate of 1°C/min, hold at -70°C for 2 min, then heat to 0°C at a rate of 1°C/min. One specimen was tested for each of these sweep tests (specimens were not retested). During each temperature sweep the specimen was subjected to a sinusoidally oscillating strain of 0.1% at a frequency of 6.28 rad/s (1 Hz). The 0.1% strain was near the upper limit of the linear viscoelastic region of the material based on an initial isothermal dynamic strain sweep test. Shear storage and loss moduli,  $G'$  and  $G''$ , respectively, and  $\tan \delta = G''/G'$  were recorded as a function of temperature.

Taking advantage of the auto-tension feature of the ARES instrument, the change in specimen length,  $\Delta L$  (i.e., gap distance), was also recorded as a function of temperature. The instantaneous coefficient of linear thermal expansion,  $\alpha$ , at a temperature,  $T$ , was estimated from the slope of the  $\Delta L$  versus  $T$  curve:

$$\alpha = \frac{1}{L_T} \frac{dL}{dT}$$

where  $L_T$  is the length of the specimen at the temperature,  $T$ , and the derivative of  $L$  with respect to  $T$  is equivalent to the derivative (slope) of  $\Delta L$  with respect to  $T$  since  $L = \Delta L + L_0$ , where  $L_0$  is the original length of the specimen (i.e., gap distance at the start of the test). This calculation is based on the assumption that the change in the gap distance with temperature represents the change in length of an unconstrained specimen. Using a parallel-plate test geometry in which the gap was automatically adjusted to maintain a fixed compressive load on the specimen, investigators previously demonstrated that the

change in gap distance was in good agreement with the dimensional change of an unconstrained specimen measured by pycnometry [1].

## RESULTS AND DISCUSSION

Results of the initial isothermal dynamic strain sweep are shown in Fig.1. The linear viscoelastic region extends slightly beyond 0.1% strain.

Values of  $G'$ ,  $G''$ , and  $\tan \delta$  for the two different temperature sweeps are shown as a function of temperature in Fig. 2. The value of  $G'$  at room temperature ( $\sim 3 \times 10^6$  Pa) is similar to that obtained previously by DMTA using an 8-mm-diameter parallel-plate test geometry ( $\sim 4 \times 10^6$  Pa) [2]. A separate DMTA study done previously using 25-mm-diameter parallel plates reported  $G' \approx 2 \times 10^5$  Pa at 30°C (0.2% strain at 6.28 rad/s) [3], which is lower than expected based on results of the current and previous studies; the low value was likely due to non-uniform specimen thickness and, hence, poor contact with the plates. Also, the parallel-plate geometry applies pure simple shearing to the sample while the torsion rectangle geometry applies a significant component of elongation. For ideal rubbers, the modulus in elongation is equal to 3 times the shear modulus, explaining some of the discrepancy.

The sharp rise in modulus as the specimen was cooled between -40 and -60°C from  $\sim 6 \times 10^6$  to  $\sim 4 \times 10^8$  Pa indicates a crystallization phase transition. The reason for the different crystallization temperatures observed in the first (-44°C) and second (-51°C) tests is unknown. Hysteresis is evident when the specimen is heated after crystallization, with melting occurring around -30°C. These crystallization and melting temperatures are higher than those obtained previously using differential scanning calorimetry (DSC): crystallization at -70°C and melting at -44°C [2]. A similar discrepancy between mechanical and calorimetric crystallization measurement techniques was previously reported [4].

Values of  $\Delta L$  and  $\alpha$  for the two temperature sweeps are plotted versus temperature in Fig. 3. On average, the calculated values of  $\alpha$  near room temperature ( $3.5 \times 10^{-4}$  to  $4.5 \times 10^{-4}$  °C<sup>-1</sup>) are slightly higher than the nominal range of  $2 \times 10^{-4}$  to  $3 \times 10^{-4}$  °C<sup>-1</sup> specified by Dow Corning [5]. Specific values of  $G'$  and  $\alpha$  at room temperature and during the crystallization transition are given in Table 1.

## ACKNOWLEDGMENTS

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Table 1:  $G'$  and  $\alpha$  at Room Temperature and Through the Crystallization Transition

	Test 1: Cool Only (25 to -100°C)			Test 2: Cool then Heat (25 to -70 to 0°C)		
	$T$ (°C)	$G'$ (Pa)	$\alpha^*$ (mm/mm-°C)	$T$ (°C)	$G'$ (Pa)	$\alpha^*$ (mm/mm-°C)
Ambient	20	$3.0 \times 10^6$	$4.5 \times 10^{-4}$	20	$3.4 \times 10^6$	$3.5 \times 10^{-4}$
Start	-40	$6.0 \times 10^6$	$4.6 \times 10^{-4}$	-46	$6.7 \times 10^6$	$3.6 \times 10^{-4}$
↓	-44	$2.0 \times 10^7$	$2.6 \times 10^{-3}$	-51	$6.9 \times 10^7$	$3.2 \times 10^{-3}$
↓	-51	$1.9 \times 10^8$	$5.5 \times 10^{-4}$	-56	$3.9 \times 10^8$	$5.3 \times 10^{-4}$
End	-55	$3.6 \times 10^8$	$2.4 \times 10^{-4}$	-60	$4.5 \times 10^8$	$2.9 \times 10^{-4}$

\* Average value based on the slope of a linear regression line through a corresponding region of the  $\Delta L$  versus  $T$  curve (see Fig. 3)

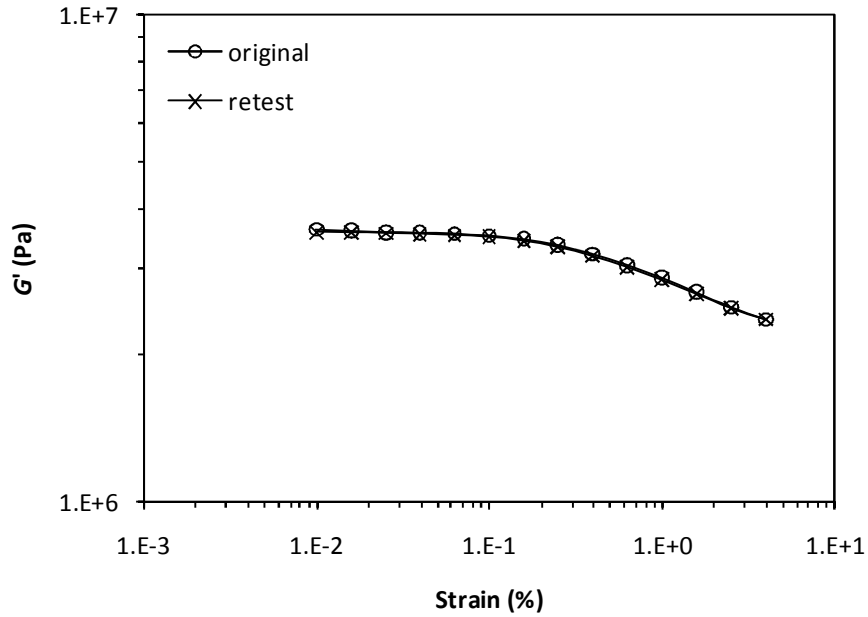


Fig. 1. Dynamic strain sweep test and retest of the same specimen at room temperature. The strain oscillated at a frequency of 6.28 rad/s (1 Hz). The linear viscoelastic region extends slightly beyond a strain of 0.1%.

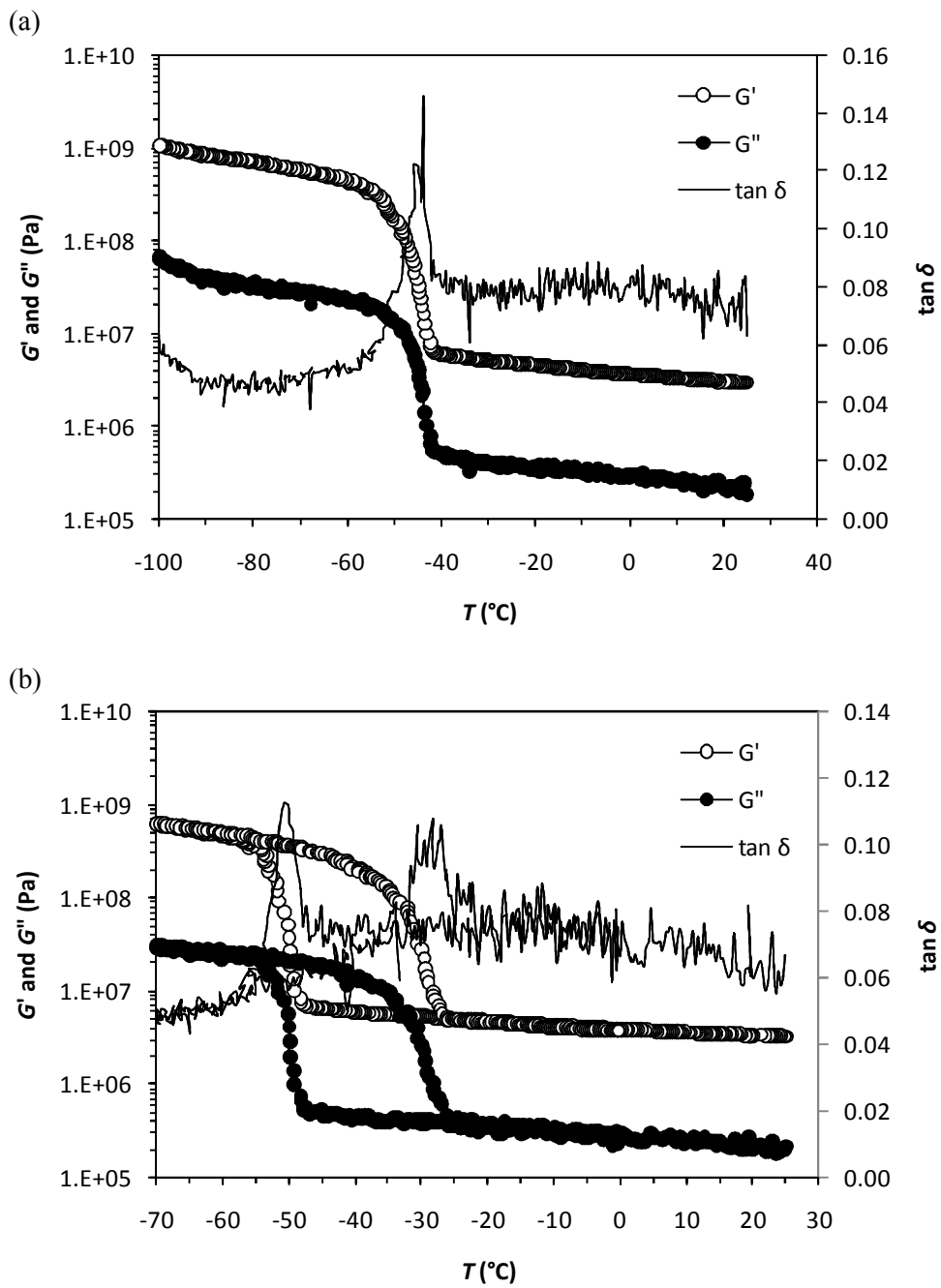


Fig. 2. Dynamic temperature sweep tests: (a) cooling and (b) cooling followed by heating. On cooling, crystallization begins between  $-40$  and  $-50^{\circ}\text{C}$ ; on heating, melting occurs around  $-30^{\circ}\text{C}$ .

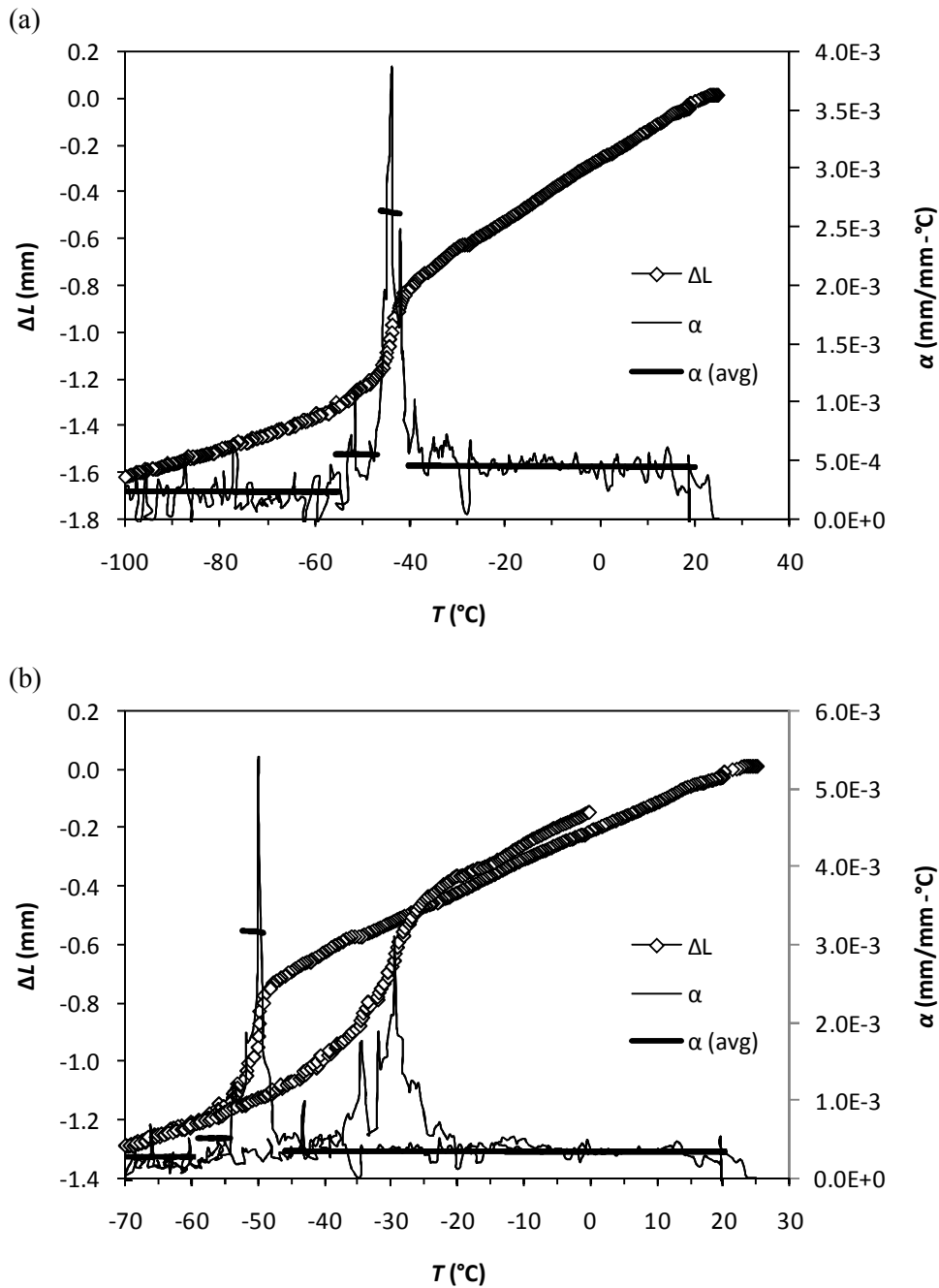


Fig. 3. Change in specimen length,  $\Delta L$ , and coefficient of linear thermal expansion,  $\alpha$ , for the two temperature sweep tests: (a) cooling and (b) cooling followed by heating. Average values of  $\alpha$  were computed for the cooling segment in each test based on the slope of a linear regression line (not shown) fit to a region of the  $\Delta L$  versus  $T$  curve.