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CHARACTERIZATION OF DC-S-2000 SILICONE RUBBER AS AN O-RING MATERIAL FOR LASER AMPLIFIER SYSTEMS

D. M. Hoffman

March 23, 1979

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ABSTRACT

We evaluated mechanical, thermal, thermodynamic, and chemical properties of Dow Corning DC-S-2000, a silicone rubber filled with silica, that was selected as an O-ring material for SHIVA laser amplifiers. We compared the properties of a batch cured in-house with the manufacturer's specifications, and we developed specific quality-control tests to evaluate future production batches of this elastomer. We also examined mechanical and thermal transitions not described in the manufacturer's bulletin. Because the silicone O-rings must function under prolonged compression, we recommend an examination of the compression properties of DC-S-2000.

INTRODUCTION

Dow Corning Silastic-S-2000 (DC-S-2000),¹ a silicone rubber filled with silica, was selected as an O-ring material for SHIVA laser amplifiers. This material is sold in an uncured state by the manufacturer, and the user or supplier cures the polymer as needed. We in the Polymeric Materials Group of the Organic Materials Division compared the properties of an experimental batch prepared in-house with the manufacturer's specifications. We then developed specific quality-control tests to evaluate future production batches of this silicone rubber. To determine potential limitations of DC-S-2000 in the particular application as an O-ring, we also examined mechanical and thermal transitions not listed in the manufacturer's bulletin.

The major component of DC-S-2000 is a silicone copolymer of dimethyl siloxane and a small amount of methylvinyl siloxane that crosslinks the polymer during the curing process:

As supplied, DC-S-2000 normally contains 2,4-dichlorobenzoyl peroxide as a vulcanizing agent. A silica filler is added (about 24% by weight) to improve mechanical properties such as modulus and tear resistance.^{2,4}

Table I lists the quality control specifications provided by Dow Corning for DC-S-2000 and the average values obtained for production lots. We found that the material we prepared and tested conformed satisfactorily to the manufacturer's specifications. Only a limited quantity of material was available, however, and the tensile strength tests described in the Dow Corning bulletin were not run.

TABLE 1. Physical and electrical properties of DC-S-2000.^{a,b}

Property	Dow Corning quality control specifications	Average values for production lots (LLL Comp 102)	ASTM test
Color	clear	clear	
Specific gravity, 25°C	1.14 ± 0.02	1.13 (1.16)	
Hardness, Shore A scale	45-60	55 (58)	D 676
Tensile strength, psi	750 ^c	1030	D 412
Elongation, %	300 ^b	530	D 412
Tear strength, psi ^d		90	D 624
Brittle point, °C		-74	D 746
Water resistance ^e			D 797
Hardness change point, °C		-20	
Water absorption, wt% change		+1.10	
Linear shrinkage, %		3.0	
Electric strength, f V/ml		540	D 149
Dielectric constant at 100 Hz		2.8	D 150
at 10000 Hz		2.8	D 150
Dissipation factor at 100 Hz		0.0003	
at 10000 Hz		0.0009	

^aRef. 1.^bProperties measured on specimens cut from slabs (0.075 in. thick) that had been press-molded for 5 min at 115°C and cured for 2 h at 250°C.^cMinimum.^dDie B.^eAfter immersion for 70 h at 100°C.^fStandard ASTM electrode (¼ in.); voltage increased at 500 V/s.

RESULTS

Table 2 summarizes the mechanical, thermal, and other properties of Comp 102, the batch of DC-S-2000 prepared at LLL. On the basis of the thermal results, we feel that use of DC-S-2000 should be limited to the temperatures between -30 and 150°C. We did not investigate the aging characteristics and compression set behavior of Comp 102.

DYNAMIC MECHANICAL PROPERTIES

The dynamic mechanical properties of DC-S-2000 were examined from -150 to 50°C on the Rheometrics Mechanical Spectrometer (RMS). Figure 1 shows the shear storage (G') and the shear

loss (G'') moduli of DC-S-2000 as functions of temperature when the specimens were mechanically stressed at a constant frequency of 10 Hz. The ratio of G''/G' , called $\tan \delta$, is also plotted on Fig. 1.

At temperatures below the glass transition point ($T_g \approx -120^\circ\text{C}$), DC-S-2000 is a brittle, semicrystalline solid. The T_g temperature corresponds to the maximum in the G'' curve in Fig. 1 and is much lower than the "brittle point" (-74°C) given in Table 1. Because the glass transition occurs over a 50°C-temperature range and depends on the frequency, dynamic mechanical measurements give a much more accurate transition temperature than the ASTM brittle point technique.

At temperatures between T_g and the melting point, DC-S-2000 is a flexible semicrystalline solid

TABLE 2. Physical characteristics of DC-S-2000 Comp 102.

Property	Value	Evaluation technique ^a
Glass transition (T_g), °C	-110 -120	DSC RMS ^b
Melting point, °C	-56 -52	DSC RMS ^b
Shear storage modulus at 30°C, MPa	13.8 ± 0.2	RMS
Shear loss modulus at 30°C, MPa	1.7 ± 0.2	RMS
Density at 25°C, g/cm ³	1.156	DGC
Crystallinity, %	63	DSC
ΔH_m , cal/g	2.86	DSC
Weight loss at 600°C, %	58.5	TGA
Swelling ratio (q) in chlorobenzene	2.36 ± 0.01	
Hardness, Shore A scale	58 ± 2	ASTM D 676
Composition, wt%		
peroxide initiator	0.16	C1 elemental analysis
silicone polymer	75.73	C elemental analysis
filler	24.11	Derived from Eq. (5)

^aDSC = Differential Scanning Calorimetry; RMS = Rheometric Mechanical Spectrometer; DGC = Density Gradient Column; TGA = Thermogravimetric Analysis.

^bTransition temperature determined from the position of the maximum in the loss modulus at 10 Hz.

FIG. 1. Shear storage modulus (G') and the shear loss modulus (G'') of DC-S-2000 Comp 102 as functions of temperature. When stressed at a constant frequency of 10 Hz, the elastomer underwent two transitions: the glass transition at about -120°C and the crystal melting point at about -52°C.

with a shear modulus only slightly less than 10^9 Pa. The elastomer melts over a fairly broad range (-50 to -30°C), as indicated by the dramatic decrease of G' and G'' as the temperature rises. Above the melting point, DC-S-2000 behaves like a vulcanized rubber, with a temperature-dependent storage modulus between 5×10^6 and 2×10^6 Pa between -30°C and room temperature. Appendix A lists the

shear storage modulus, loss modulus, and tan delta values from Fig. 1 as functions of temperature.

Figure 2 shows the dynamic shear modulus as a function of frequency at 30°C. At this temperature, neither the shear storage modulus nor the loss modulus varies significantly over three decades of frequency, indicating that under ambient operating conditions, DC-S-2000 should be stable to

mechanical vibrations encountered in the laser amplifier system. The dynamic viscosity ($N' = G''/\omega$, where ω is the angular frequency) is also plotted in Fig. 2. Appendix B tabulates the shear modulus and dynamic viscosity values as functions of stressing frequency at 30°C.

THERMAL PROPERTIES

Figure 3 illustrates a representative differential scanning calorimeter (DSC) curve of Comp 102 that shows the thermal transitions of the polymer. In this type of thermal measurement, the glass transition point is indicated by a discontinuity in the heat capacity; for Comp 102, it occurred at about -110°C. The melting temperature (T_m) is defined as the intersection of the slope of the melting endotherm with the isothermal baseline. In Fig. 3, T_m is -56°C. The heat of melting (ΔH_m , in cal/g of

elastomer) is proportional to the area under the melting-endotherm curve, calculated from the relation

$$\Delta H_m = \int_{T_i}^{T_f} \left(\frac{dQ}{dT} \right) dT = \frac{KA_p \Delta T_s T_s}{W_p a}, \quad (1)$$

where K is the instrument constant (0.144 cal/°C-min), ΔT_s and T_s are, respectively, the x- and y-axis sensitivities of the instrument in °C/in., a is the heating rate in °C/min, and W_p is the weight of the polymer. The value of ΔH_m for DC-S-2000 is 2.86 cal/g.

FIG. 2. Dynamic mechanical properties of DC-S-2000 Comp 102 at 30°C as functions of stressing frequency. These analyses showed no excessive changes in shear storage modulus (G'), shear loss modulus (G''), or dynamic viscosity (N') when the sample was subjected to mechanical vibration at normal operating temperatures.

FIG. 3. Typical differential scanning calorimeter (DSC) curve of DC-S-2000 Comp 102 silicone rubber. This trace shows the glass transition temperature (T_g) as a discontinuity in the heat capacity at -125°C . As the temperature rose, the T_g was followed by a crystallization exotherm at about -103°C and a broad melting endotherm of approximately 2.86 cal/g between about -60 to -40°C .

The percent crystallinity (X_c) of the sample below the melting point is

$$X_c = \Delta H_m / \Delta H_f, \quad (2)$$

where ΔH_f is the heat of fusion (in cal/g) of a perfectly crystalline polymer of dimethyl siloxane (4.57 cal/g).⁵ Using Eq. (2), we calculated that DC-S-2000 Comp 102 is about 63% crystalline.

THERMAL STABILITY

We used thermogravimetric analysis (TGA) to estimate the thermal stability of DC-S-2000. At a heating rate of 10°C/min , the elastomer began to volatilize very slowly at about 190°C (Fig. 4). An unidentified additive, constituting approximately 8 wt% of the elastomer, volatilized between 350 and 400°C . This material was probably a silicone of low molecular weight present as a solvent for the initiator or used to wet the filler.

Above 450°C , most of the polymer degraded within 2 h; above 600°C , no weight was lost and 41.5 wt% of nonvolatile residue remained. We could not estimate the filler content using this technique

because the nonvolatile residue contained both silica filler and polymer degradation products. On the basis of this analysis, we recommend that DC-S-2000 not be used above 150°C .

OTHER PROPERTIES

Swelling Measurements

The quantity of solvent absorbed by a crosslinked polymer is constant for a given solvent in a polymer of constant crosslink density. The swelling ratio $q = V_s/V_0$ reflects the extent of vulcanization of the polymer. Because DC-S-2000 contains silica as a filler, the initial volume V_0 depends on the filler content. The degree of crosslinking and the filler content are interdependent, and the swelling ratio therefore cannot be used to monitor changes in the degree of crosslinking unless the filler concentration is known. Because the filler content can be estimated from elemental analysis, the swelling ratio can be used to indicate variations in crosslink density. For Comp 102, the swelling ratio was 2.36.

FIG. 4. Thermogravimetric analysis of DC-S-2000 Comp 102 showing a slow loss of weight above 190°C.

Density

Density measurements made using the density gradient column (DGC) technique at 30°C gave an average value of 1.156 g/cm³ for Comp 102 samples. This density was within the specific-gravity limits indicated by the manufacturer (1.14 ± 0.2 g/cm³).

Shore A Hardness

Shore A hardness of Comp 102, measured using the ASTM test D 676, was 58 ± 2 . This value was somewhat higher than the average (55) measured by the manufacturer for production lots (Table 1), but it falls below the upper limit (60) listed in the specifications.

Elemental Analysis for Metals

We used flame ionization spectrometry to identify trace metals in Comp 102 and found measurable amounts of magnesium, calcium, boron, copper, and aluminum (Table 3). These were probably impurities contained in the filler rather than metallic catalysts added by the manufacturer. Table 3 lists all elements for which the elastomer was analyzed and the quantities found; for those elements not detected, the limits of the tests are given.

Elemental Analysis for C, H, N, and Cl

Because the crosslinking initiator 2,4-dichlorobenzoyl peroxide is the only chlorine-

containing species in DC-S-2000, an estimate of the weight fraction of peroxide initiator (W_i) can be obtained from the weight fraction of chlorine (W_{Cl}) in the elastomer. The relationship is

$$W_i = 2.674 W_{Cl} \quad (3)$$

If no carbon is present in the filler, then the weight fraction of polysiloxane in the elastomer (W_p) is approximately

$$W_p = 3.086 W_C - 3.648 W_{Cl} \quad (4)$$

where W_C is the weight fraction of all carbon in the elastomer. It is assumed in Eq. (4) that the carbon in the polymer comes solely from dimethyl siloxane rather than from the methylvinyl siloxane copolymer; we assumed the error introduced by this simplification is small because the methylvinyl siloxane copolymer is only a minor component. The weight fraction of filler (W_f) in the elastomer is then

$$\begin{aligned} W_f &= 1 - W_i - W_p \\ &= 1 - 3.086 W_C + 0.974 W_{Cl} \end{aligned} \quad (5)$$

Table 2 gives the weight fractions of the three Comp 102 components; Table 3 lists the results of the C, H, N, and Cl analyses.

TABLE 3. Chemical analysis of DCS-2000 Comp 102.^a

Element	Concentration ^b	
	ppm	wt%
Ca	<6	
B	2	
Al	<2	
Cu	<0.6	
Mg	<0.6	
Na	(<200)	
Cd, Pb	(<60)	
Ba, Nb, Cr, Mo, Zn, Sn, Sb, Bi	(<20)	
Zr, V, Fe	(<6)	
Ti, Co, Ni	(<2)	
Be, Sr, Mn, Ag	(<0.6)	
C		0.2461
H		0.0600
N		0.0001
Cl		0.0006

^aDetermined by flame ionization spectrometry.^bValues in parentheses give the detection limits for elements that were not found.

CONCLUSIONS

Simple tests such as Shore A hardness (ASTM D 676), tensile strength (ASTM D 412), and solvent swelling tests should be sufficient to verify the quality of production lots of DC-S-2000 silicone rubber and to identify undesired changes in formulation. Elastomer batches that do not meet the manufacturer's specifications should be rejected as unsuitable O-ring material, and drastic deviation of test results from the test limits should prompt a more detailed analysis of the batch.

Because only a limited quantity of Comp 102 was available, we could not measure the tensile strength, but we believe that this test should be conducted on future samples of DC-S-2000. We also

feel that, because the silicone O-rings must function under prolonged compression, the results of a compression set test (ASTM D 395) of DC-S-2000 would be of interest. On the basis of the observed thermal stability of this material, however, we suggest that compression-test temperatures should not exceed 85°C.

We recommend that the Laser Group run the Shore A hardness, solvent swelling, and tensile strength tests on future lots of DC-S-2000 to maintain quality control standards. Special problems with DC-S-2000 should be referred to the Polymeric Group of the Organic Materials Division for analysis and proposed solutions.

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APPENDIX A **DYNAMIC MECHANICAL PROPERTIES OF DC-S-2000 COMP 102** **AS FUNCTIONS OF TEMPERATURE**

Shear storage modulus (G') and shear loss modulus (G'') of DC-S-2000 Comp 102 as functions of temperature while subjected to mechanical vibration (10 Hz).

Temperature, °C	G', Pa	G'', Pa	tan delta
-147.390	0.23498E 10	0.10345E 09	0.1140
-147.590	0.23556E 10	0.10135E 09	0.0430
-142.590	0.23354E 10	0.10282E 09	0.0440
-137.990	0.23177E 10	0.10436E 09	0.0450
-134.390	0.23022E 10	0.11039E 09	0.0480
-133.490	0.22700E 10	0.11586E 09	0.0510
-128.890	0.21916E 10	0.13605E 09	0.0621
-123.790	0.20284E 10	0.17283E 09	0.0852
-119.590	0.18924E 10	0.19560E 09	0.1034
-119.090	0.15797E 10	0.21256E 09	0.1348
-114.590	0.12063E 10	0.17738E 09	0.1471
-109.790	0.99292E 09	0.13688E 09	0.1379
-97.9991	0.95332E 09	0.12462E 09	0.1307
-105.090	0.81165E 09	0.92107E 08	0.1135
-100.290	0.71631E 09	0.74762E 08	0.1004
-95.6991	0.65290E 09	0.66823E 08	0.1024
-95.3991	0.64492E 09	0.63402E 08	0.0983
-90.6991	0.58097E 09	0.57113E 08	0.0983
-85.7991	0.52228E 09	0.52927E 08	0.1013
-81.2990	0.48288E 09	0.48445E 09	0.1003
-81.3990	0.47704E 09	0.46897E 08	0.0983
-76.5991	0.42142E 09	0.42278E 08	0.1003
-71.9991	0.36863E 09	0.37731E 08	0.1024
-66.9991	0.33843E 09	0.35324E 08	0.1044
-66.7990	0.33001E 09	0.32777E 08	0.0993
-61.7990	0.27462E 09	0.28664E 08	0.1044
-57.3990	0.22108E 09	0.23299E 08	0.1054
-52.5990	0.19557E 09	0.21798E 08	0.1115
-52.2990	0.16770E 09	0.17503E 08	0.1044
-47.5000	0.86769E 08	0.97585E 07	0.1125
-42.6990	0.30370E 08	0.40632E 07	0.1338
-38.7990	0.13142E 08	0.19190E 07	0.1460
-38.1990	0.43946E 07	0.59238E 06	0.1348
-33.0000	0.44350E 07	0.65211E 06	0.1470
-28.3990	0.42845E 07	0.42118E 06	0.0983
-21.8990	0.40904E 07	0.59307E 06	0.1450
-23.0000	0.41020E 07	0.49456E 06	0.1206
-18.2990	0.35462E 07	0.37013E 06	0.1044
-13.5000	0.34043E 07	0.36566E 06	0.1074
-2.7990	0.37873E 07	0.42593E 06	0.1125

APPENDIX B **DYNAMIC MECHANICAL PROPERTIES OF DC-S-2000 COMP 102** **AS FUNCTIONS OF FREQUENCY AT 30°C**

Shear storage modulus (G'), shear loss modulus (G''), and dynamic viscosity (N') of DC-S-2000 Comp 102 as functions of frequency.

Frequency, rad/s	G' , Pa	G'' , Pa	N' , Pa-s
9.9902E 01	1.3929E 06	1.7784E 05	1.7802E 03
6.2831E 01	1.3648E 06	1.5626E 05	2.4869E 03
3.9734E 01	1.2494E 06	1.5318E 05	3.8552E 03
2.5051E 01	1.1761E 06	1.2870E 05	5.1377E 03
1.5795E 01	1.1525E 06	1.1213E 05	7.0992E 03
9.9588E 00	1.1433E 06	1.0319E 05	1.0361E 04
6.2831E 00	1.1358E 06	9.7919E 04	1.5584E 04
3.9734E 00	1.1299E 06	1.0082E 05	2.5375E 04
2.5051E 00	1.1193E 06	9.1987E 04	3.6719E 04
1.5795E 00	1.1104E 06	9.1252E 04	5.7769E 04
9.9588E 01	1.1071E 06	8.4304E 04	8.4653E 04
6.2831E 01	1.0932E 06	8.3246E 04	1.3249E 05
3.9734E 01	1.0848E 06	8.4787E 04	2.1338E 05
2.5051E 01	1.0770E 06	8.0920E 04	3.2302E 05
1.5795E 01	1.0698E 06	7.7155E 04	4.8844E 05
9.9902E 02	1.0607E 06	7.3303E 04	7.3374E 05
1.5795E 01	1.0761E 06	7.9775E 04	8.0504E 05
2.5051E 01	1.0825E 06	7.9163E 04	3.1601E 05
3.9734E 01	1.0904E 06	8.0834E 04	2.0343E 05
6.2831E 01	1.1036E 06	8.2922E 04	1.3197E 05
9.9588E 01	1.1110E 06	8.1244E 04	8.1580E 04
1.5795E 00	1.1211E 06	8.7616E 04	5.5467E 04
2.5051E 00	1.1317E 06	8.9589E 04	3.5762E 04
3.9734E 00	1.1424E 06	9.2735E 04	2.3338E 04
6.2831E 00	1.1510E 06	9.6904E 04	1.5422E 04
9.9588E 00	1.1558E 06	1.0079E 05	1.0121E 04
1.5795E 01	1.1616E 06	1.1068E 05	7.0072E 03
2.5051E 01	1.1732E 06	1.1533E 05	4.6040E 03
3.9734E 01	1.2287E 06	1.4317E 05	3.6031E 03
6.2831E 01	1.3132E 06	1.5833E 05	2.5199E 03
9.9588E 01	1.3916E 06	1.9752E 05	1.9834E 03
9.9902E 01	1.3852E 06	1.8249E 05	1.8267E 03