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Synopsis of Mechanical Aging and Fatigue Testing of Llama50 Ink for Direct-Ink-Write 3D Printing

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Overview

This document provides a brief synopsis of the results of mechanical aging (thermal and radiation) and fatigue testing of Llama50, an LLNL-made 50A durometer siloxane resin for direct-ink-writing (DIW) with low-temperature capability. Aging studies were performed on both bulk and DIW printed specimens. The fatigue test was performed on DIW printed specimens.

Short-Term Compression Set of Aged Bulk Llama50

Llama50 was cast into solid button specimens (n=4). The buttons were cured at 150°C for 1 hr in the mold using a hot press (in air). The buttons were removed from the mold and baked at 150°C for 16 hrs under nitrogen. The thickness of the buttons, h_0, was measured. The buttons were aged under 25% compressive engineering strain (ε=0.25) at 70°C for 70 hrs under nitrogen according to ASTM D395. The buttons were then allowed to cool uncompressed for 30 minutes, and the thickness, h_t, was measured. Compression set relative to deflection (*i.e.,* aging strain) was calculated using the formula

$$\text{Relative CS [\%]} = 100\times(h_0-h_t)/\varepsilon h_0 \quad (1)$$

A 3-cycle compressive load-deflection test was performed before and after aging. The load at the aging strain before aging, F_0, and after aging, F_t, was used to calculate the load retention:

$$\text{LR [\%]} = 100\times F_t/F_0 \quad (2)$$

Average relative compression set and load retention are shown in Table 1. Values are reported for buttons cast from typical size batch as well as from a larger-scale batch.

Table 1: Short-Term Relative Compression Set and Load Retention of Bulk Llama50

Relative Compression Set (%)	Load Retention (%)
5.1±0.2 (typical batch), 6.5±0.5 (large batch)	85.9±1.0 (large batch) F_0 = 697 N (1089 kPa), F_t = 599 N (935 kPa)

Compression Set and Load Retention of Aged DIW Printed Llama50

A 5-layer spaced hexagonal close packed (sHCP) structure was 3D printed using the DIW technique. The strand diameter was 250 µm and the center-to-center spacing was 375 µm. The porosity of the structure was ~20%. The material was cured for 16 hrs at 150°C in air. Disc specimens were cut from the sample and aged under ~10% compressive engineering strain at 25°C, 40°C, 55°C or 70°C under nitrogen (n=2 at each temperature). The compressed thickness during aging was 0.760±0.005 mm defined by the thickness of the steel spacers used in the aging fixtures. The change in spacer thickness due to thermal expansion is negligible (~0.0006 mm at 70°C). Before aging and at various timepoints during aging, thickness was measured and a 3-cycle compressive load-deflection test was performed on the specimens. The specimens cooled under compression for 24 hrs and were measured immediately after removal from the aging fixtures. Compression set relative to deflection and load retention were calculated using Eq. 1 and Eq. 2, respectively. Results up to the 1-year timepoint are shown in Fig. 1.

The isothermal curves were shifted in time using time-temperature superposition (TTS) to provide a long-term prediction (Fig. 2). A bootstrap-mean-minimum-arc algorithm[1,2] was used to shift the curves.

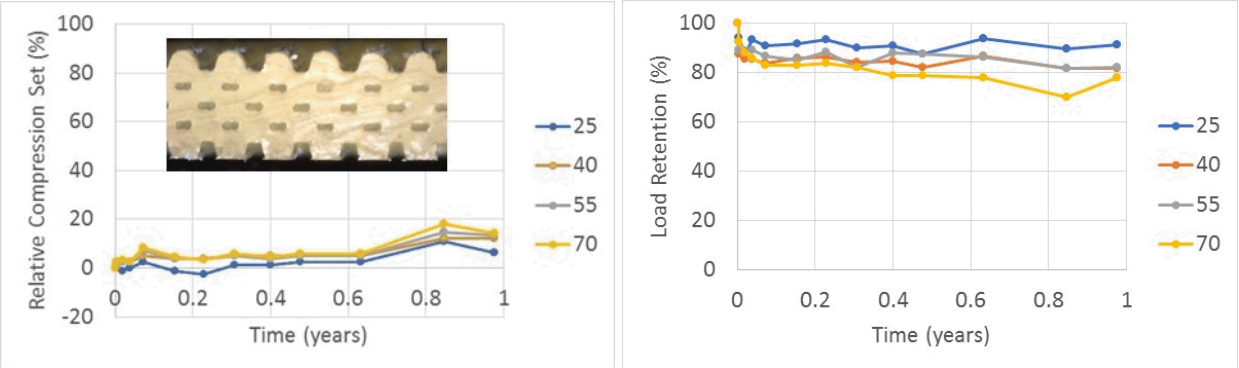

Fig. 1. Relative compression set and load retention of sHCP Llama50 aged at 25°C, 40°C, 55°C or 70°C (average of n=2 specimens). A cross-section of the sHCP structure is shown in the inset.

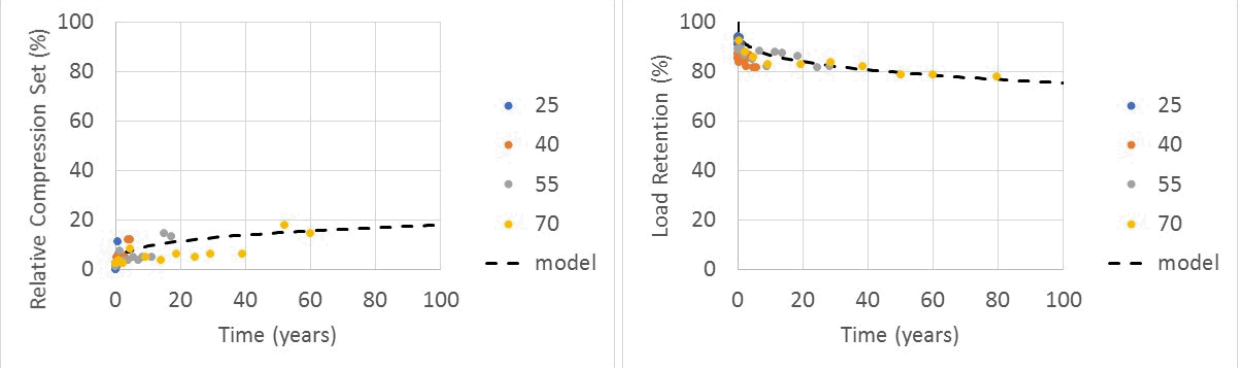

Fig. 2. Long-term TTS predictions of relative compression set and load retention of sHCP Llama50.

The data in Fig. 1 and Fig. 2 were acquired immediately after the specimens were removed from the aging fixtures. A subsequent experiment in which specimens were aged under ~10% compressive engineering strain at 70°C for 1 week showed that thickness and load recover over time. Rapid recovery occurred within the first 6 hrs of relaxation, with maximum recovery after ~24 hrs (Fig. 3).

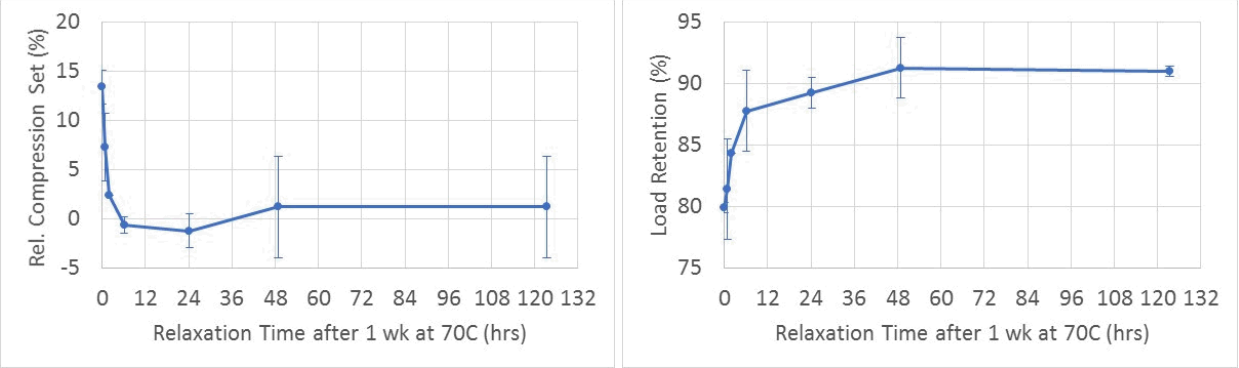

Fig. 3. Recovery of compression set and load retention of sHCP Llama50 over time (average of n=2 specimens).

Printed sHCP specimens were exposed to gamma radiation (Co-60, dose rate ~0.04 Mrad/hr) while under ~10% compressive engineering strain at ambient temperature under vacuum (n=4 per dose). Average relative compression set and load retention measured after the specimens relaxed uncompressed for 30 minutes are shown in Table 2.

Table 2: Relative Compression Set and Load Retention of Irradiated sHCP Llama50

Radiation Dose (Mrad)	Time Under Compression[(a)] (hrs)	Relative Compression Set (%)	Load Retention (%)
0.1	~5	5±1	107±3
1	~27	10±2	100±1
0 (non-irrad)	*~5*	*0[(b)]*	*~99[(b)]*
0 (non-irrad)	*~27*	*0[(b)]*	*~96[(b)]*

(a) Includes time in aging fixture before and after irradiation
(b) Extrapolated from 25°C data in Fig. 1 (measured immediately after removal from fixtures); no measurement at 5 or 27 hrs of compression (earliest measurement at 48 hrs of compression: 24 hrs in oven plus 24 hrs cooling)

Radiation-induced stiffening resulted in high load retention despite the compression set. For non-irradiated specimens under compression for the same amount of time, the estimated compression set was zero. Therefore, the compression set is due to radiation-induced crosslinking.

Fatigue Testing of DIW Printed Llama50

A 5-layer sHCP structure was 3D printed using the DIW technique. The strand diameter was 250 µm and the center-to-center spacing was 375 µm. The porosity of the structure was ~20%. The material was cured for 16 hrs at 150°C in air. A disc specimen (~0.85-mm-thick) was cut from the sample and subjected to 250,000 compressive loading cycles to 1000 kPa. The compressed thickness at maximum stress remained around 0.7 mm during the test (Fig. 4), indicating no physical damage.

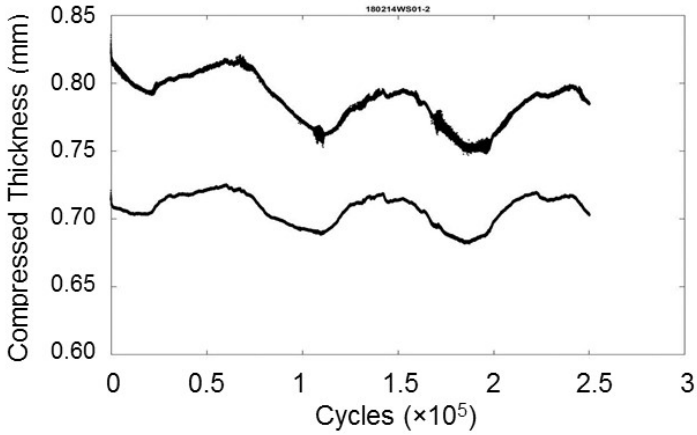

Fig. 4. Fatigue test of sHCP Llama50 (250,000 loading cycles to 1000 kPa). The upper curve is the compressed thickness at zero load and the lower curve is the compressed thickness at 1000 kPa.

Tensile Properties and Hardness of Aged Bulk Llama50

Llama50 was cast into 2-mm-thick sheets. Each sheet was cured at 150°C for 1 hr in the mold using a hot press (in air). Each sheet was removed from the mold and baked at 150°C for 16 hrs under nitrogen. The material was put into ovens at 35°C, 70°C, and 85°C under nitrogen. At various timepoints material was removed from the ovens and ASTM D638 Type IV dog bones (n=5) were cut using a die. Young's modulus, tensile strength, elongation at break (based on initial grip separation), and hardness (durometer Type A) were measured (test speed = 33 mm/min). The results are shown in Fig. 5.

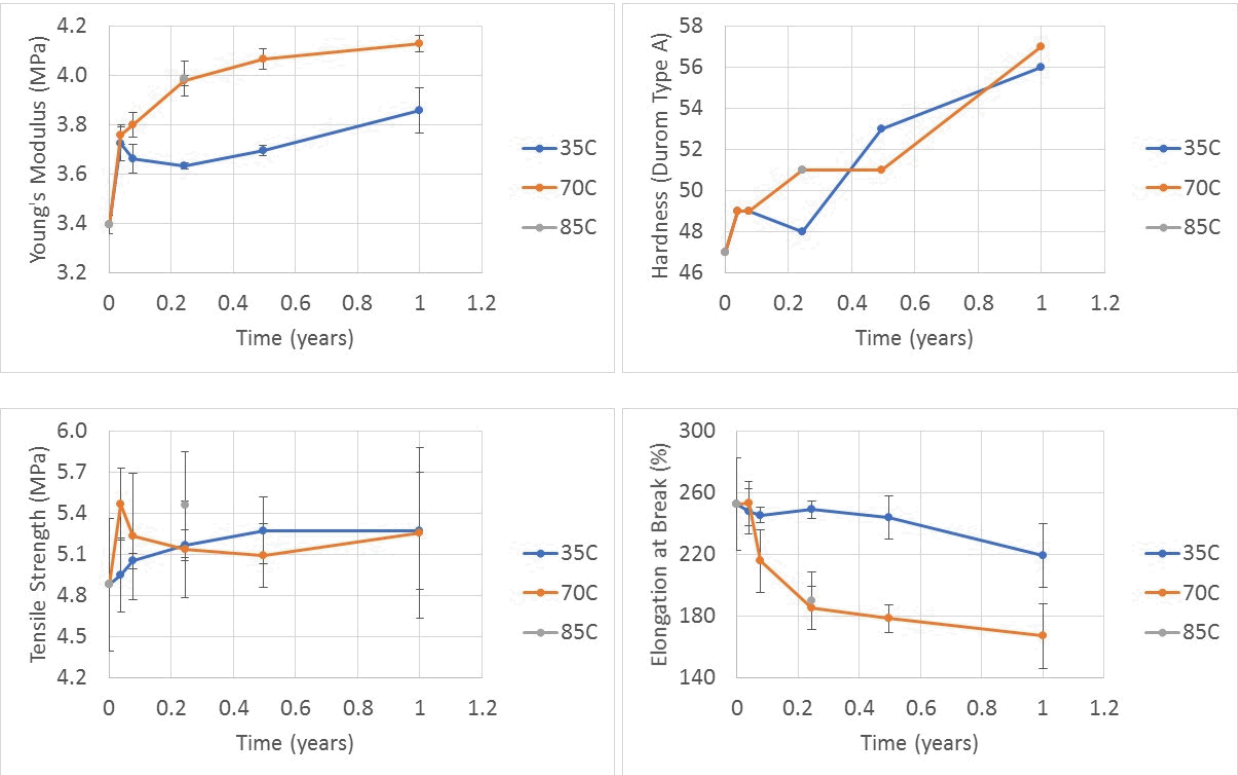

Fig. 5. Effect of thermal aging on tensile properties and hardness of bulk Llama50 (average of n=5 specimens). There is only a single data point for 85°C (3-month timepoint).

Bulk dog bone specimens were exposed to gamma radiation (Co-60, dose rate ~0.04 Mrad/hr) at ambient temperature under vacuum (n=5 per dose). The effect of irradiation on tensile properties and hardness is shown in Table 3. Radiation-induced hardening is evident, causing the specimens to become more brittle with increasing dose.

Table 3: Effect of Radiation on Hardness and Tensile Properties of Bulk Llama50

Radiation Dose (Mrad)	Hardness (Durometer Type A)	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
0	47	3.40±0.04	4.88±0.48	253±30
0.1	48	3.47±0.06	5.10±0.38	246±20
1	50	3.72±0.04	5.30±0.14	216±6

References

1. A. Maiti. A geometry-based approach to determining time-temperature superposition shifts in aging experiments. Rheol Acta 55, 83-90 (2016).
2. A. Maiti, *et al*. Long-term property prediction from the accelerated aging of initiator powder and foam support cushions. LLNL-PRES-759701 (2018).