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Thermal Aging Study of a Dow Corning SE 1700 Porous Structure Made by Direct Ink Writing: 1-Year Results and Long-Term Predictions

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Thermal aging study of a Dow Corning SE 1700 porous structure made by direct ink writing: 1-year results and long-term predictions

Ward Small, Mark A. Pearson, Amitesh Maiti, Thomas R. Metz, Eric B. Duoss, Thomas S. Wilson

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SUMMARY

Dow Corning SE 1700 (reinforced polydimethylsiloxane) porous structures were made by direct ink writing (DIW). The specimens (~50% porosity) were subjected to various compressive strains (15, 30, 45%) and temperatures (room temperature, 35, 50, 70°C) in a nitrogen atmosphere (active purge) for 1 year. Compression set and load retention of the aged specimens were measured periodically during the study. Compression set increased with strain and temperature. After 1 year, specimens aged at room temperature, 35, and 50°C showed ~10% compression set (relative to the applied compressive deflection), while those aged at 70°C showed 20-40%. Due to the increasing compression set, load retention decreased with temperature, ranging from ~90% at room temperature to ~60-80% at 70°C. Long-term compression set and load retention at room temperature were predicted by applying time-temperature superposition (TTS). The predictions show compression set relative to the compressive deflection will be ~10-15% with ~70-90% load retention after 50 years at 15-45% strain, suggesting the material will continue to be mechanically functional. Comparison of the results to previously acquired data for cellular (M97*, M9760, M9763) and RTV (S5370) silicone foams suggests that the SE 1700 DIW porous specimens are on par with, or outperform, the legacy foams.

MATERIALS AND METHODS

Sample Preparation

Dow Corning SE 1700 clear adhesive is a two-part heat cure reinforced polydimethylsiloxane rubber with a 10:1 by weight mix ratio. After mixing using a Thinky planetary mixer, the resin was vacuum degassed, loaded into a 30 cc syringe, vacuum degassed again, and centrifuged. The trapped air was bled from the syringe and a micronozzle (250 µm inner diameter) was attached to the syringe. The syringe was mounted to the z-stage of a three-axis linear positioning system (Aerotech).

The porous samples were made using a direct ink write (DIW) 3D printing process [1]. A silicon substrate coated with a teflon mold release agent was mounted on the xy-stage of the positioning system. A positive displacement fluid dispenser (Ultimus IV Model 2800-30, Nordson) was connected to the syringe and programmed to dispense the resin at a constant rate that matched the print speed (15 mm/s). Printing was initiated by executing the tool path program in the A3200 CNC Operator Interface Control software (Aerotech). An eight-layer structure resembling a face-centered tetragonal (FCT) configuration was printed (Fig. 1). The filament diameter was 250 µm and the filament center-to-center spacing was 500 µm. The finished sample was ~75 mm square by ~1.6 mm thick. The silicon substrate with the completed sample was removed from the positioning system and placed in an oven at 150°C for 1 h under nitrogen purge to cure the resin. The cured sample was detached from the silicon substrate and a 28.68 mm diameter die was used to cut out circular disk specimens from the sample. The specimens were purged with nitrogen for 24 h at room temperature immediately before use.

Accelerated Aging and Data Acquisition

Specimens were compressed in rigs comprised of two parallel steel platens bolted together and separated by spacers with thickness to achieve the desired compressive aging strain; one specimen per compression rig. Two specimens were compressed at each nominal aging strain (15, 30, or 45%) and aging temperature (room temperature, 30, 50, or 70°C). The actual aging strains varied slightly since the specimen thicknesses varied slightly while the spacer thicknesses were constant. Heated aging was conducted in ovens under active nitrogen purge. Room temperature aging was also conducted under active nitrogen purge. At specific time points (24 h, 1 week, 2 weeks, 4 weeks, and monthly thereafter to 12 months), the uncompressed specimen thickness and load at the aging strain were measured using an Instron 5500R dual-column load frame. Heated specimens were allowed to cool under compression for 24 h prior to measurement in an air atmosphere. The compression rig containing the specimen was positioned in the Instron (air atmosphere) and the bolts were removed while under compressive load. Three unload-load cycles were performed (test speed = 0.2 mm/min), and the load and crosshead displacement were recorded at 10 Hz. The bolts were put back in place and aging of the compressed specimen under nitrogen was resumed. Instrument compliance (~10^{-4} mm/N) was determined using an empty compression rig to correct the crosshead displacement.

Data Analysis: Compression Set, Load Retention, and Time-Temperature Superposition

A schematic diagram illustrating measurement of compression set and load retention using the Instron load frame is given in Appendix A. The recovered thickness of the uncompressed specimen (*i.e.*, final thickness t_f) was determined based on the compliance-corrected displacement of the crosshead when the load first began to increase during the third loading phase. Compression set S (relative to compressive deflection) was calculated using the measured original specimen thickness t_o, compressed thickness t_c, and final thickness t_f: $S=(t_o-t_f)/(t_o-t_c)=(t_o-t_f)/\varepsilon t_o$. The force F_t measured just before the upper platen of the compression rig made contact with the spacer (seen as a spike in the force) during the third loading phase was used to calculate the load retention. Load retention R was calculated by dividing the force measured while the specimen was under compression by that at time zero (before aging): $R=F_t/F_0$.

The original specimen thickness t_0 used to calculate compression set was measured using the Instron (see Appendix A) for the specimens aged at room temperature. For the other specimens, the original thickness was measured using a digital thickness gauge (Ono Sokki EG-233) with an 8 mm diameter flat contact point at a constant force of 40.7 g (7.9 kPa compressive stress), and the measurement was reduced by an offset to estimate the thickness measured using the Instron (an offset of 0.012 mm was determined from the room temperature specimens which were measured using both methods). Estimating the thickness in this manner is not expected to significantly affect the calculated compression set values. However, in future studies, the original thickness of all specimens should be measured in a manner that is consistent with the method of measuring the thickness after aging (in this case, using the Instron with the specimen in the compression rig with the bolts removed).

After 14 months, the specimens were removed from the compression rigs and their final thickness was measured using the digital gauge after a relaxation period of 30 minutes, and the final compression set was calculated using the original and final thicknesses measured using the digital gauge (Appendix B). This measurement was done to verify that the Instron-derived compression set values calculated during the study for the non-room temperature aged specimens were reasonable given the method of estimating the original thickness.

The time zero force F_0 was measured using the Instron (see Appendix A) for the specimens aged at room temperature, but not for the other specimens. For the other specimens, F_0 was estimated using a curve fit to the load vs. deflection data (corrected for instrument compliance) collected from a separate specimen

made using the same DIW process. The force at the aging strain for each specimen was determined from the curve fit to the data. Due to variability in the load deflection between printed samples, estimating F_0 in this manner is expected to introduce some amount of error in the calculated load retention values. Further, the aging strain used to determine F_0 from the curve fit was estimated for the non-room temperature specimens since it was calculated using an estimation of the original thickness. To ensure proper calculation of load retention in future studies, F_0 should be measured for each specimen prior to aging using the same method of measuring the force as is used during aging (in this case, using the Instron with the specimen in the compression rig with the bolts removed).

Time-temperature superposition (TTS) was applied to the compression set and load retention data to predict the long-term response at room temperature. The room temperature, 30, 50, and 70°C isotherms were graphically shifted horizontally (by eye) along the time axis to generate a master curve at a reference temperature of 25°C (room temperature). Assuming an Arrhenius relationship between the multiplicative shift factor a_T and the temperature, the natural log of a_T was plotted as a function of $1/RT$, where R=8.31 J/mol-K is the gas constant and T is the absolute temperature, and the activation energy E_a was determined from the slope (slope = $-E_a$). An automated TTS shifting method was later developed to reduce the subjectivity of shifting by eye (Appendix C).

Comparison to Legacy Materials

The results are compared to those from previous aging studies using similar compression rigs on legacy silicone foams: M97* (LLNL study), M9760 (KCP study), and M9763 (LLNL and KCP studies) cellular foams and S5370 RTV foam (LLNL study). At KCP, the M9760 and M9763 foams were subjected to 20, 35, or 50% compressive strain at room temperature, 50, or 70°C for 8.5 years in air (30-60% relative humidity) [2-Schneider]. Load retention was measured using the method employed in the current study; compression set was not measured. At LLNL, the M97* foam was subjected to 15, 30, or 55% compressive strain and the M9763 foam was subjected to 25% compressive strain in a nitrogen atmosphere at the same temperatures used in the current study for 2 years; compression set and load retention were measured using the methods employed in the current study. There appears to be a discontinuity in the LLNL M9763 70°C data after the first year; the validity of the second year data at this temperature is suspect and was not used in the TTS predictions. The experimental setups of the LLNL and KCP tests are summarized in Table 1.

RESULTS AND DISCUSSION

Compression Set

Relative compression set over 1 year is shown in Fig. 2. After 1 year, specimens aged at room temperature, 35, and 50°C showed ~10% compression set, while those aged at 70°C showed 20-40% depending on the aging strain. Comparison of the results to previously acquired data for cellular (M97*, M9763) and RTV (S5370) silicone foams suggests that the SE 1700 DIW porous specimens outperform the legacy foams. The TTS master curves (Fig. 3) predict relative compression set will be ~10-15% after 50 years at 15-45% strain (E_a = 96 kJ/mol), suggesting the material will continue to be mechanically functional. Comparison of the results to previously acquired TTS master curves for cellular (M97*, M9763) and RTV (S5370) silicone foams suggests that the SE 1700 DIW porous specimens outperform the legacy foams (Fig. 4).

The relative compression set after 14 months calculated using the original and final specimen thickness measured using the digital gauge is shown in Appendix B. The values are in decent agreement with the Instron-derived values acquired after 1 year.

Load Retention

Load retention over 1 year is shown in Fig. 5. Due to the increasing compression set, load retention decreased with temperature, ranging from ~90% at room temperature to ~60-80% at 70°C. Comparison of the results to previously acquired data for cellular silicone foams (M97*, M9760, M9763) suggests that the SE 1700 DIW porous specimens are on par with the legacy foams. The TTS master curves (Fig. 6) predict ~75-90% load retention after 50 years at 15-45% strain (E_a = 140 kJ/mol), suggesting the material will continue to be mechanically functional. The activation energy for load retention appears to be higher than that for compression set, suggesting different mechanisms for the two processes. Comparison of the results to previously TTS master curves for cellular silicone foams (M97*, M9763) suggests that the SE 1700 DIW porous specimens are on par with, or outperform, the legacy foams (Fig. 7).

The master curves for the SE 1700 DIW porous specimens obtained by the new automated shifting method are shown in Appendix C. They are in good agreement with those obtained by shifting by eye.

The relationship between compression set and load retention for specimens aged at 30% compressive strain is illustrated in Fig. 8. As expected, load retention decreases as compression set increases.

Other Observations

All of the specimens aged at 30°C showed yellow discoloration around the outer perimeter; none of the other specimens exhibited discoloration. One of the specimens aged at 50°C under 45% compressive strain adhered to the lower plate of the compression rig such that the specimen was damaged when removing it; all other specimens were removed without incurring damage.

Methodology Issues and Suggestions for Future Studies

Several methodology issues may impact the results of this study:

- Because the specimens were not removed from the compression rigs, the upper plate of the compression rig always exerted a stress (8.5 kPa) on the specimen during measurement of specimen thickness and load at maximum strain using the Instron. Therefore, slightly underestimated values of thickness and load were used to calculate compression set and load retention.
- The Instron was used to measure the thickness of the aged specimens and the original thickness of the room temperature specimens, but not the original thickness of the non-room temperature specimens. Therefore, the Instron-derived original thickness of the non-room temperature specimens used to calculate compression set was estimated from values obtained using a digital thickness gauge (~0.012 mm difference between the two methods).
- The time zero force F_0 used to calculate load retention was not measured for the non-room temperature specimens. Therefore, it was estimated using load-deflection data from a separate DIW sample which likely did not perfectly agree with the specimens in this study.
- Force F_t at the aging strain is determined from the "knee" where the upper platen of the compression rig contacts the spacer (see Appendix A). This "knee" is not perfectly sharp, so there is some subjectivity in determining its location on the curve, particularly for the 45% compression which approached lock-up.

Suggestions for future studies:

- Include time zero Instron measurements of all specimens. If the specimens will remain in the compression rig during measurement, they should be measured in the same manner at time zero.
- If the specimens can be removed from the compression rigs during the aging study without suffering damage due to excessive adhesion, measurement will be simplified. The Instron could be equipped

with parallel platens (one spherical seat to ensure parallelism) and the crosshead displacement zeroed with the platens touching each other (zero gap). Load-deflection data of the specimen would be acquired without interference by the spacers. Specifically, the force F_t at the aging strain could be taken directly from the load-deflection data instead of estimating from the "knee." Further, since the load-deflection curve would not need to be shifted horizontally such that the "knee" is at zero displacement and there is no extra stress imparted on the specimen by the rig, the thickness could be taken as the crosshead displacement at a nominal stress (*e.g.*, 2 kPa).

- If the specimens cannot be removed from the compression rigs without incurring damage due to excessive adhesion, the specimens could be sandwiched between two thin metal shims before being compressed in the rigs. The sandwiched specimens (including the potentially adhered shims) could be removed from the rigs for measurement in the Instron.
- The compression rigs could be coated with Teflon by the LLNL Plastics Shop to prevent specimen adhesion.

CONCLUSIONS

Compression set and load retention measured after accelerated (thermal) aging suggest the DIW porous structure (FCT, 250 μm filament diameter, 500 μm center-to-center spacing, 8 layers) made from Dow Corning SE 1700 will retain mechanical functionality after 50 years. Comparison of the results to previously acquired data for cellular (M97*, M9760, M9763) and RTV (S5370) silicone foams, suggests that the SE 1700 DIW porous specimens are on par with, or outperform, the legacy foams.

ACKNOWLEDGMENTS

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2. JW Schneider. ESP – Data from restarted life tests of various cellular silicone materials – 2007. Honeywell FM&T Report KCP-613-8357 (2007).

Appendix A

Method of Measuring Compression Set and Load Retention

The compression rig containing the specimen (Fig. A1) is loaded into the Instron load frame. The upper adjustable 3-point contact test fixture is brought into contact with the upper platen of the rig and the bolts are removed. Three unload-load cycles are performed and the third load is used to calculate the specimen thickness and load at maximum compression (Fig. A2). The specimen thickness measured in the compression fixture by the Instron is slightly underestimated since the upper platen of the fixture (mass = 0.560 kg) always sits on top of the 28.68 mm diameter specimen, resulting in a compressive stress of 8.5 kPa and, hence, some degree of compression.

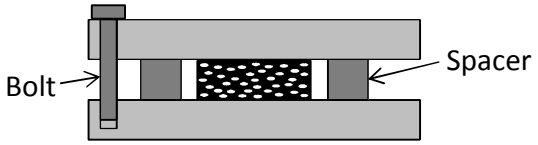


Fig. A1. Schematic diagram of a specimen in the parallel plate compression rig. The two platens were bolted together with the metal spacers providing a fixed compressive strain.

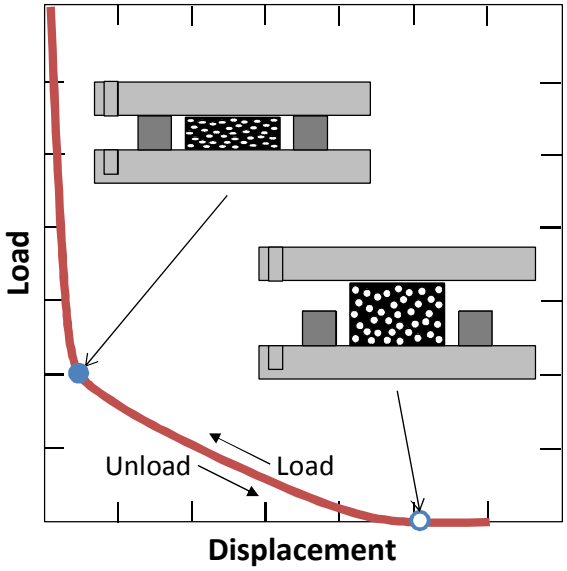


Fig. A2. Schematic diagram of the load versus displacement during the unload-load cycles. Only a single curve is shown which represents any of the loading phases. The open circle indicates the point at which the load begins to increase during loading. If the displacement is set to zero when the specimen is fully compressed (closed circle), the open circle displacement is added to the spacer thickness to calculate the thickness of the uncompressed specimen. This value is used to calculate the compression set. Note that the entire curve may be shifted slightly horizontally to bring the closed circle to zero displacement if necessary. The closed circle indicates the point at which the specimen is fully compressed during loading (just before the load spikes when the upper platen contacts the metal spacer). The closed circle load is divided by the original closed circle load at time zero (before aging) to calculate the load retention. Note that the load imparted on the specimen by the upper platen of the compression rig is ignored.

Appendix B

Comparison of Digital Gauge-Derived and Instron-Derived Relative Compression Set

After 14 months, the specimens were removed from the compression rigs and their final thickness was measured using the digital gauge after a relaxation period of 30 minutes, and the final compression set was calculated using the original and final thicknesses measured using the digital gauge. This measurement was done to verify that the Instron-derived compression set values calculated during the study for the non-room temperature aged specimens were reasonable given the method of estimating the original thickness. The values are in decent agreement with the Instron-derived values acquired after 1 year (Fig. B1). Note that a 5.5 mm flat contact point at a constant force of 31.3 g (12.9 kPa compressive stress) was used for the 14 month thickness measurement and an 8 mm diameter flat contact point at a constant force of 40.7 g (7.9 kPa compressive stress) was used for the original (time zero) thickness measurement.

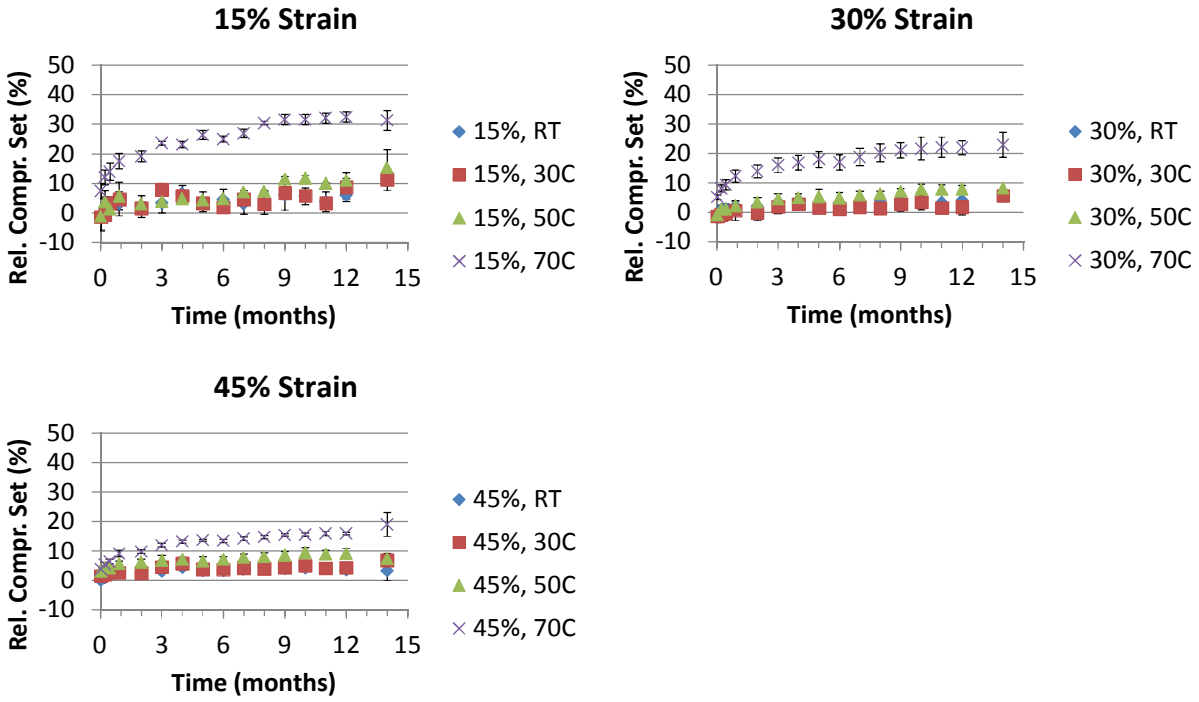


Fig. B1. Digital gauge-derived relative compression set at 14 months plotted with the Instron-derived values over 1 year.

Appendix C

TTS Master Curves Obtained by Automated Shifting

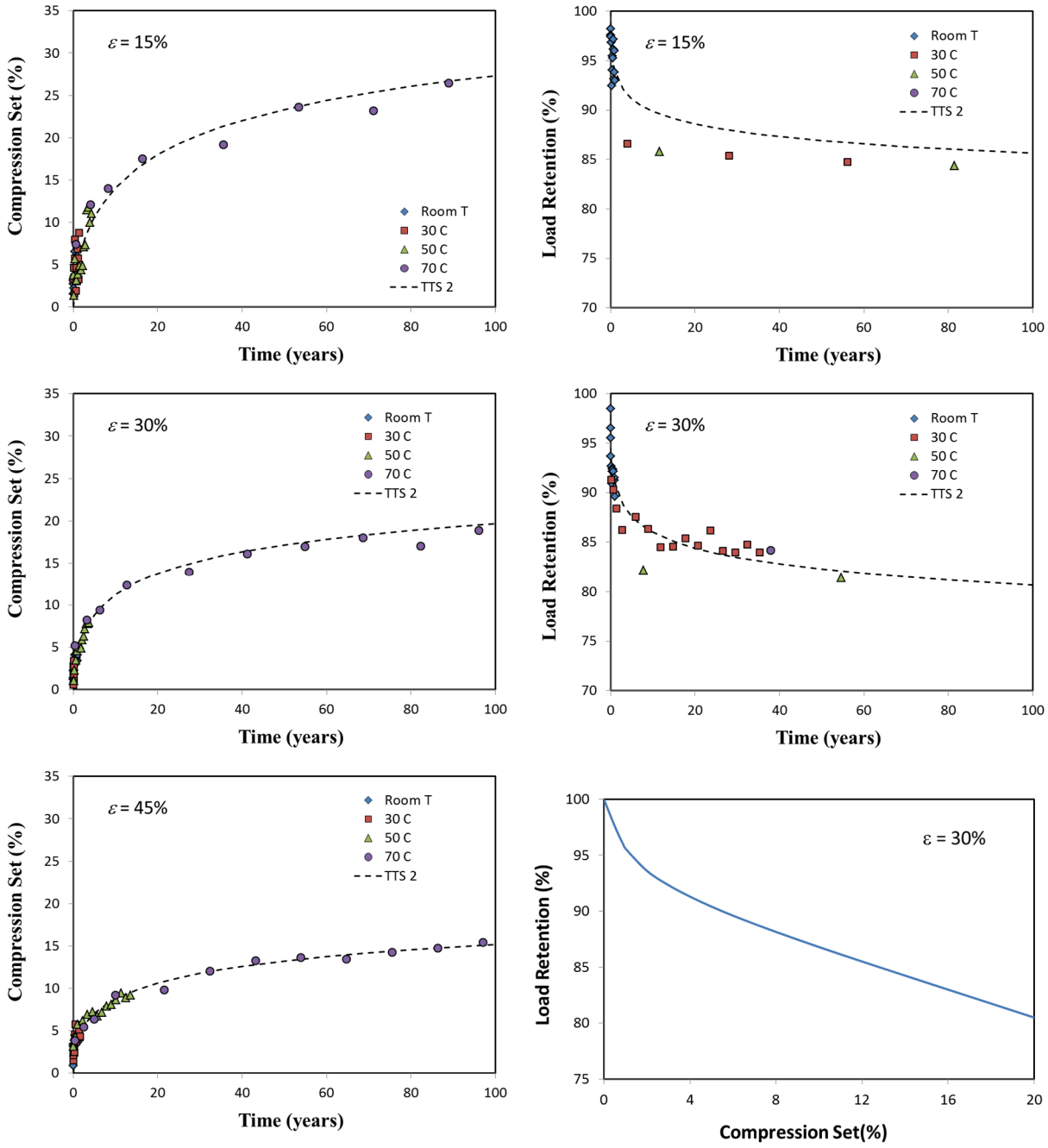


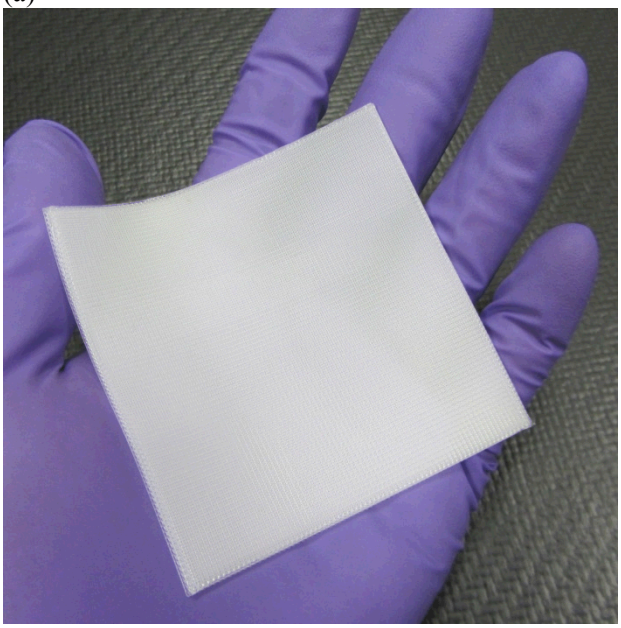
Fig. C1. TTS master curves of relative compression set and load retention obtained by automated shifting for the SE 1700 DIW porous specimens. The load retention data at 45% aging strain was not amenable to shifting and is not shown. Curve fits are given by the dashed lines. Load retention as a function of relative compression set for 30% aging strain (based on the fits to the master curves) is also shown. These automated TTS results are in good agreement with those obtained by shifting by eye.

Table 1: Setup for LLNL and KCP Thermal Aging Tests

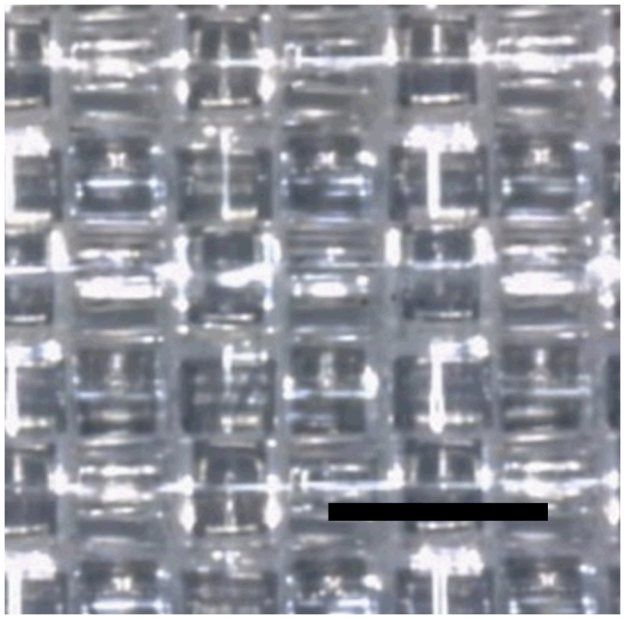
	LLNL SE 1700	**LLNL M97***	**LLNL M9763**	**LLNL S5370**	**KCP M9760**	**KCP M9763**
Dates of Study	Sep 2013 – Sep 2014	Nov 2010 – Nov 2012	Dec 2005 – Mar 2008[(a)]	Dec 2005 – Mar 2008[(a)]	Oct 1998 – Apr 2007	Oct 1998 – Apr 2007
Aging Duration	1 year	2 years	2 years	2 years	8.5 years	8.5 years
Aging Atmosphere	Nitrogen (dry); active purge	Nitrogen (dry); active purge	Nitrogen (dry); active purge	Nitrogen (dry); active purge	Air (30-60% RH)	Air (30-60% RH)
Specimen Diameter	1.129 in (28.68 mm)	1.129 in (28.68 mm)	1.0 in (25.4 mm)	1.0 in (25.4 mm)	?	?
Thickness of Single Specimen	0.065 in (1.64 mm)	0.12 in (3.05 mm)	0.039 in (1.0 mm)	0.035 in (0.9 mm)	0.040 in (1.0 mm)	0.040 in (1.0 mm)
Nominal Porosity	50%	60%	63%	~25% (high density)	60%	63%
Multiple Specimens Stacked in Fixture?	No	No	Yes (3 specimens alternating with 4 steel spacers)	Yes (3 specimens alternating with 4 steel spacers)	?	?
Compressive Strain During Aging	15%, 30%, 45%	15%, 30%, 55%	25%	25%	20%, 35%, 50%	20%, 35%, 50%
Spacer Block Thickness	15%: 0.057 in (1.45 mm) 30%: 0.047 in (1.19 mm) 45%: 0.037 in (0.94 mm)	15%: 0.102 in (2.59 mm) 30%: 0.084 in (2.13 mm) 55%: 0.054 in (1.37 mm)	Steel spacer: 0.0629 in (1.597 mm) Spacer block: 0.339 in (8.61 mm)	Steel spacer: 0.0629 in (1.597 mm) Spacer block: 0.329 in (8.36 mm)	?	?
Aging Temperature	RT, 35°C, 50°C, 70°C	RT, 35°C, 50°C, 70°C	RT, 35°C, 50°C, 70°C	RT, 35°C, 50°C, 70°C	RT, 50°C, 70°C	RT, 50°C, 70°C
Instron Test Speed	0.2 mm/min	0.2 mm/min	0.2 mm/min	0.2 mm/min	?	?
Values Measured	Compression set, load retention	Compression set, load retention	Compression set, load retention	Compression set, load retention	Load retention	Load retention

[(a)]Study was interrupted for several months, then resumed

(a)



(b)



(c)

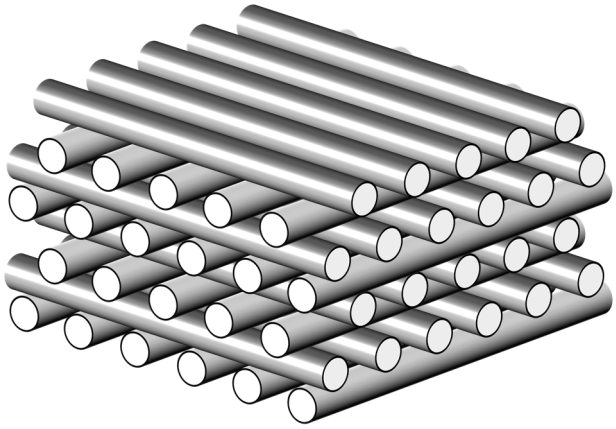
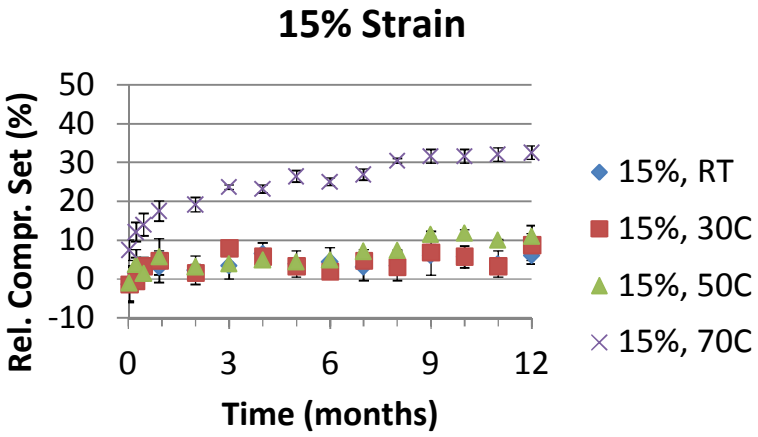


Fig. 1. (a) Photograph and (b) top-view micrograph of a DIW printed SE 1700 porous sample (bar = 0.5 mm). (c) Illustration of the eight-layer FCT structure.

(a)



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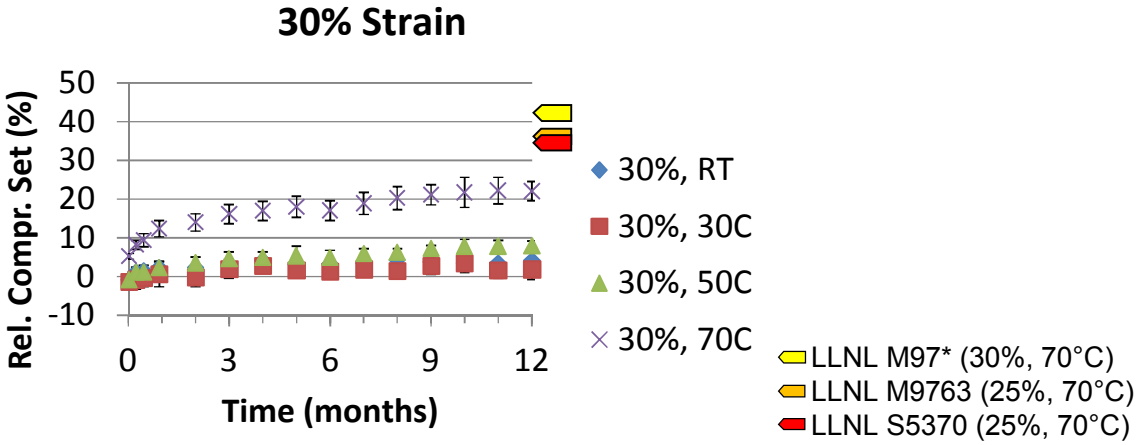

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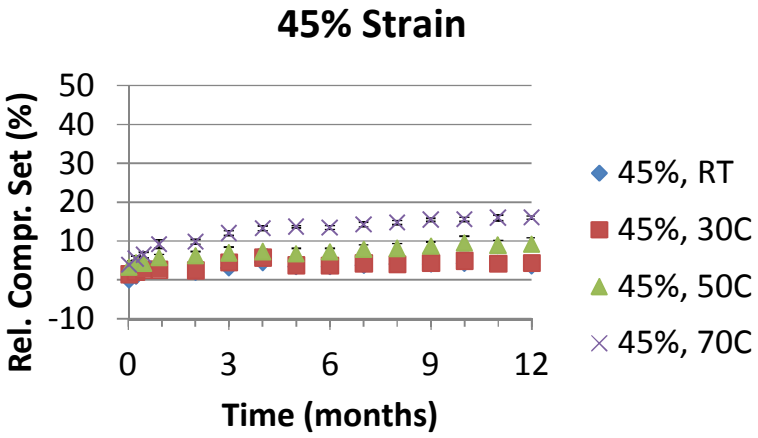


Fig. 2. Compression set (relative to deflection) of DIW printed SE 1700 porous specimens thermally aged under (a) 15%, (b), 30% and (c) 45% compressive strain. 1-year values of compression set of legacy foams aged under 25-30% compression at 70°C are shown for comparison in (b).

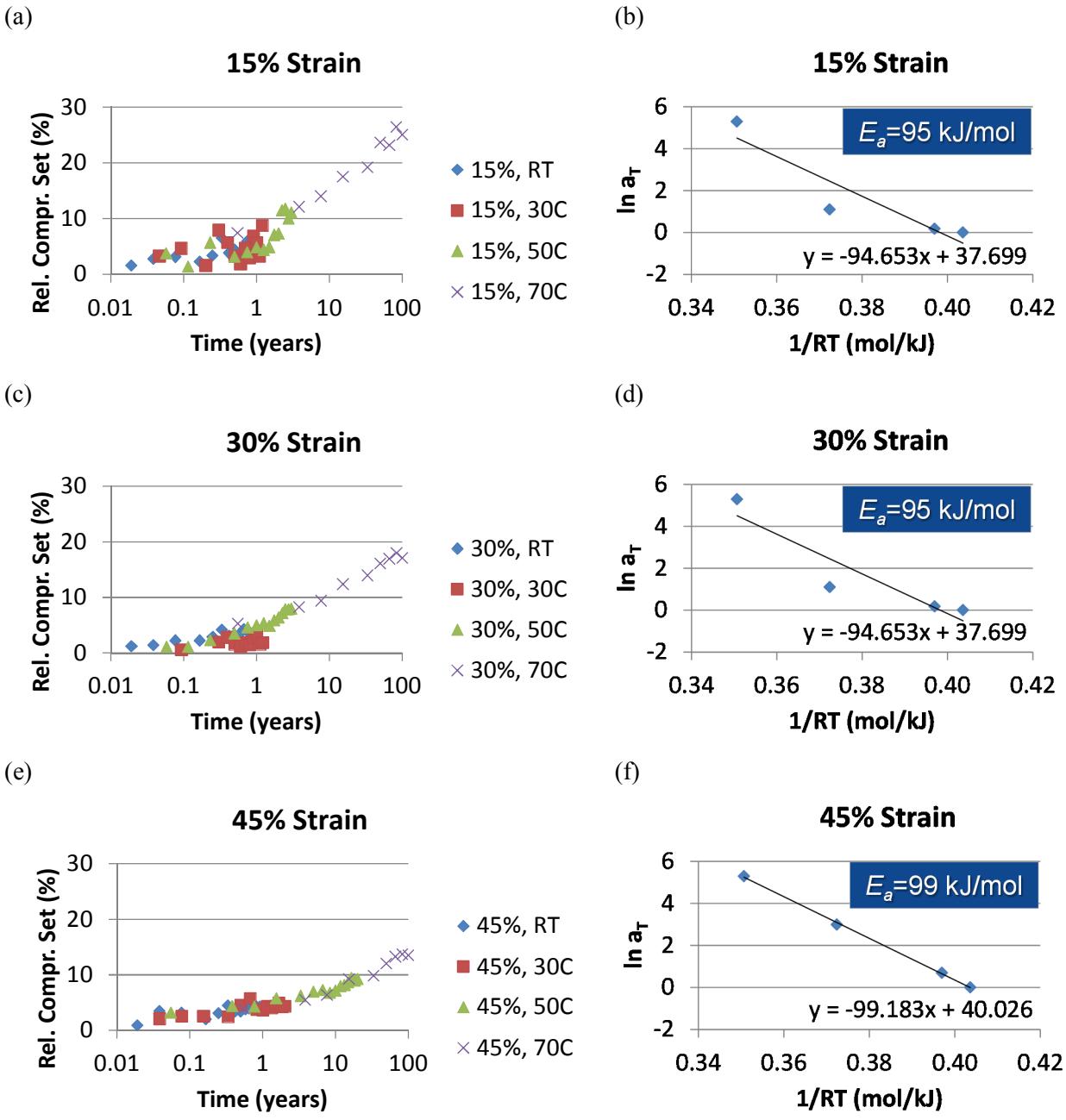


Fig. 3. Room temperature TTS master curves of relative compression set for aging strains of (a) 15%, (c) 30%, and (e) 45% for DIW printed SE 1700 porous specimens. The associated Arrhenius plots and activation energies E_a are shown in (b), (d), and (f), respectively.

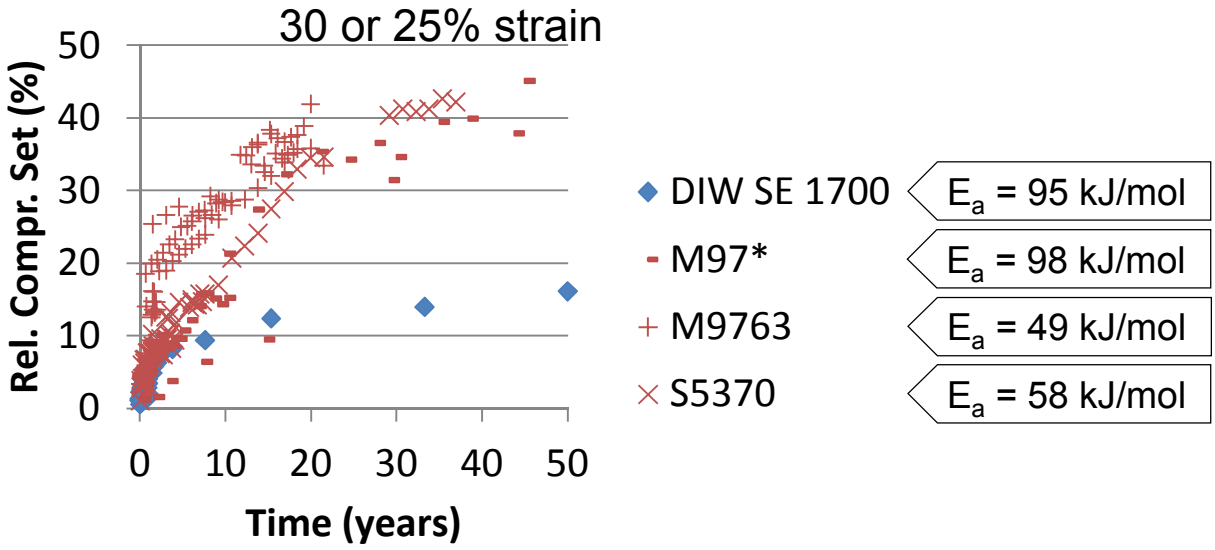
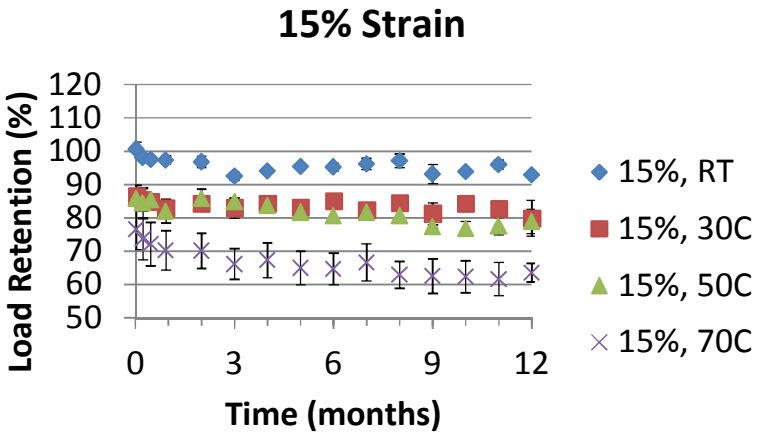
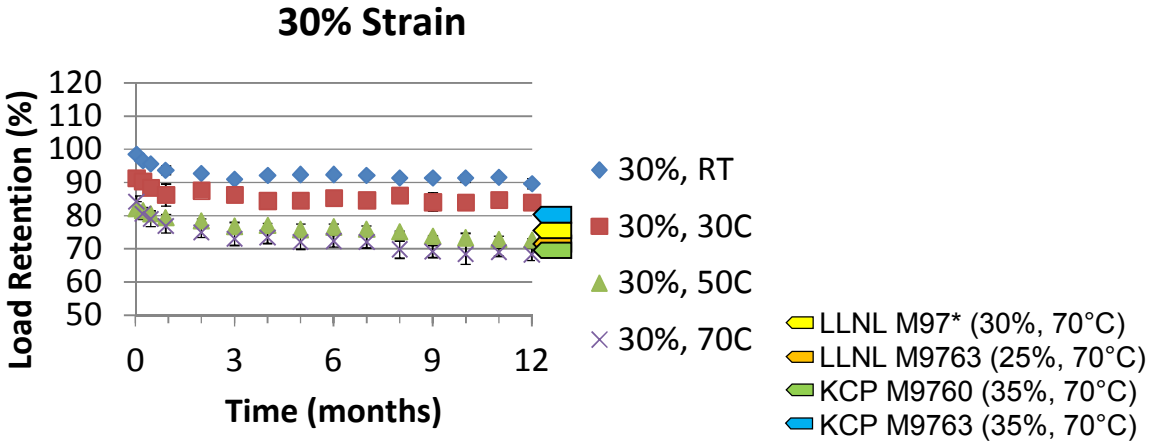


Fig. 4. Room temperature TTS master curve of relative compression set for 30% aging strain for DIW printed SE 1700 porous specimens compared to TTS master curves of previously tested legacy foams thermally aged under 25-30% compression. Activation energies E_a are shown.

(a)



(b)



(c)

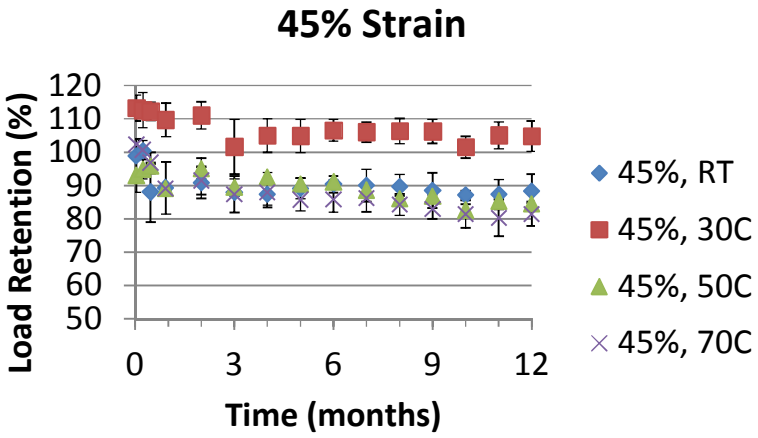


Fig. 5. Load retention of DIW printed SE 1700 porous specimens thermally aged under (a) 15%, (b), 30% and (c) 45% compressive strain. 1-year values of load retention of legacy foams aged under 25-35% compression at 70°C are shown for comparison in (b).

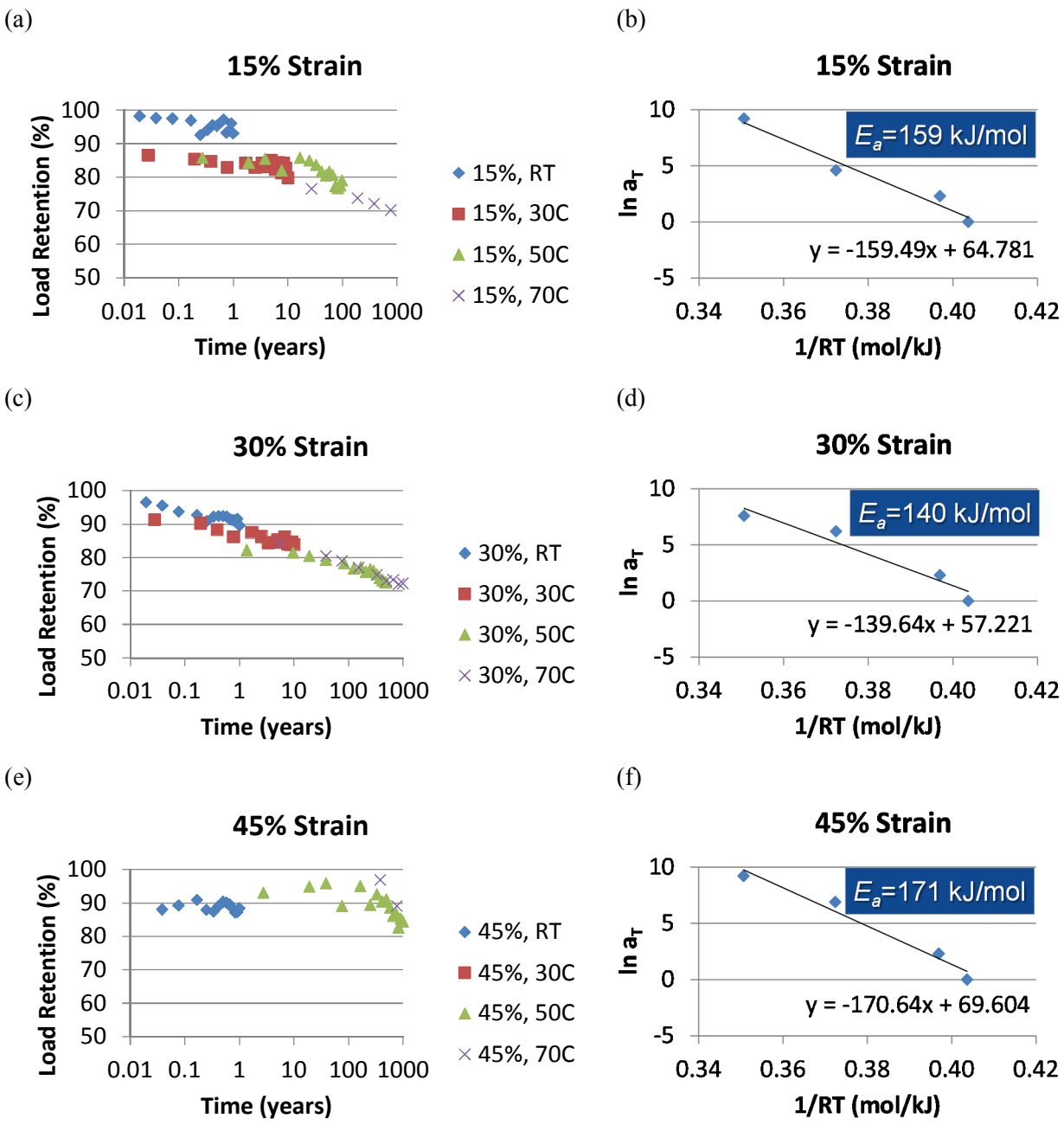


Fig. 6. (a) Room temperature TTS master curves of load retention for aging strains of (a) 15%, (c) 30%, and (e) 45% for DIW printed SE 1700 porous specimens. The associated Arrhenius plots and activation energies E_a are shown in (b), (d), and (f), respectively. Master curves of previously tested legacy foams thermally aged under 25-30% compression are shown for comparison in (b) and (f).

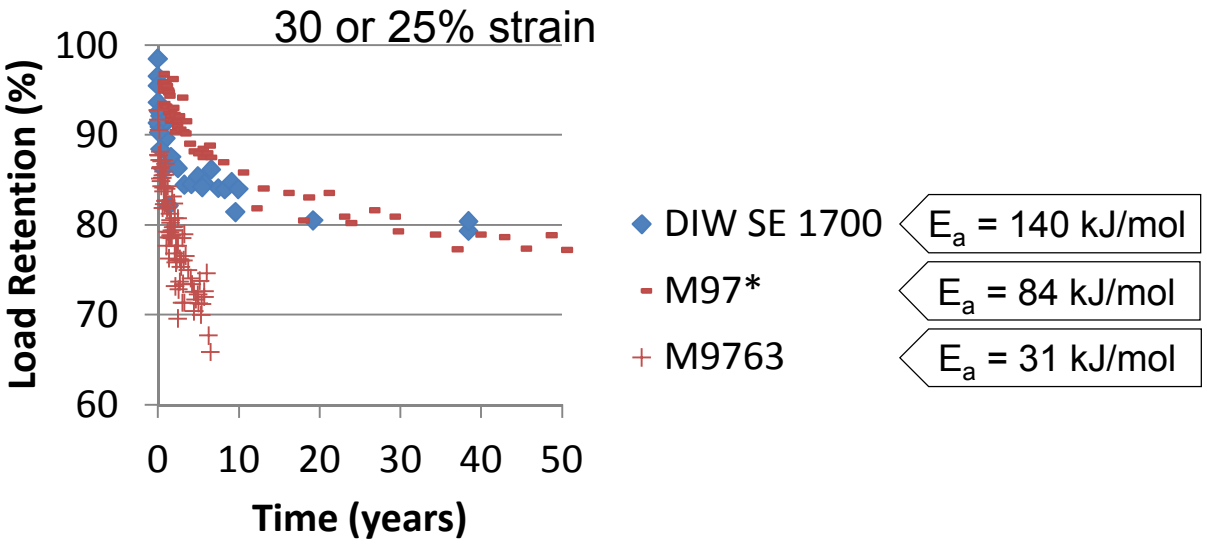


Fig. 7. Room temperature TTS master curve of load retention for 30% aging strain for DIW printed SE 1700 porous specimens compared to TTS master curves of previously tested legacy foams thermally aged under 25-30% compression. Activation energies E_a are shown.

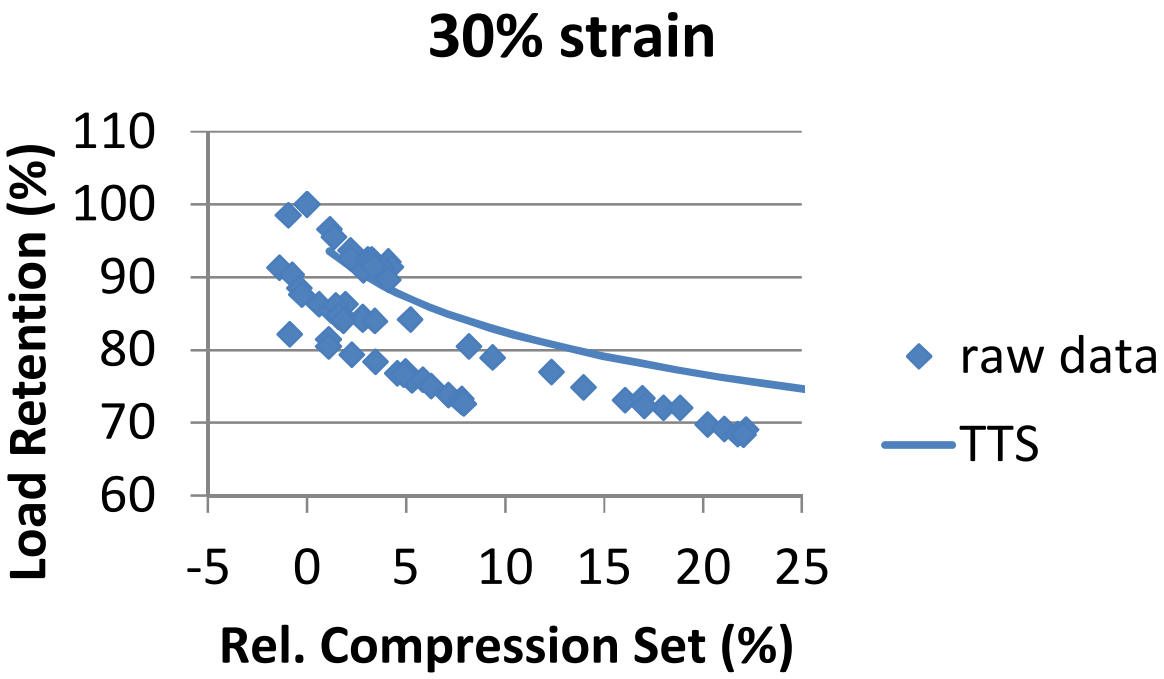


Fig. 8. Relationship between compression set and load retention for 30% aging strain (at all temperatures) for DIW printed SE 1700 porous specimens. The solid line was obtained by fitting curves to the compression set and load retention TTS master curves.