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2022 Status Report - Fiberboard Properties and Degradation Rates for Storage of 9975 Shipping Package in KAC

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September 2022

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EXECUTIVE SUMMARY

Thermal, mechanical, and physical properties have been measured on fiberboard samples following accelerated aging for up to 17 years. The aging environments include elevated temperature up to 250 °F (the maximum allowed service temperature for fiberboard in 9975 packages) and elevated humidity. Accelerated aging results have been analyzed and used to build aging models. Correlations relating several properties (thermal conductivity, energy absorption, weight, dimensions, and density) to their rate of change in potential storage environments have been developed. Combined with an estimate of the actual conditions the fiberboard experiences in K-Area Complex (KAC), these models allow development of service life predictions.

KAC completed calculations that supported extending the service life of 9975 packages with 3013 containers in storage from 20 years to 40 years. These calculations addressed the potential for degraded fiberboard properties following 40 years in storage using degradation models developed previously. Due to differences in containers, 9975 packages with non-3013 containers are only approved for 20 years of storage. The updated degradation models developed in this report have been compared to the assumptions in those calculations, and the current results for fiberboard dimensions, density, radial thermal conductivity, and energy absorption remain consistent with those calculations. The axial thermal conductivity degradation rate slightly exceeds calculations estimate of 0.5% per year between 130 and 160 °F. Additional data will continue to be collected to permit future refinements to the models and assumptions.

Some of the predicted degradation rates presented in this report are extreme. However, these relate to environments that do not exist within KAC or would be postulated only as upset conditions that would not likely persist for an extended period. For a typical package stored in KAC with approximately 10-12 watts internal heat load or less, and ambient temperatures below 90 °F, the fiberboard assemblies experience storage conditions less severe than any of the aging environments. Fiberboard in conforming packages with lower internal heat loads should experience little or no degradation and is expected to provide a service life beyond the currently approved 40 year storage period. Packages with higher internal heat loads may not continue to perform their required safety functions beyond 40 years. Ultimately, service life will be determined by the cumulative effect of degradation from all the conditions these packages might encounter.

The results and model predictions presented in this report are applicable to 9975 packages with cane or softwood fiberboard overpack assemblies. These degradation models do not address the effects of non-conforming conditions such as the presence of excess moisture and mold or beetle infestations.

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LIST OF ABBREVIATIONS

DE	Destructive examination
ID	Inside diameter
KAC	K-Area Complex
OD	Outside diameter
RH	Relative humidity
SARP	Safety analysis report for packaging
SCV	Secondary containment vessel
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
WME	Wood moisture equivalent

1.0 Introduction

Savannah River Site (SRS) stores plutonium materials within model 9975 shipping packages in the K-Area Complex (KAC). The 9975 shipping package consists of a 35 gallon stainless steel drum, Celotex[®] fiberboard insulation, lead shield, and primary and secondary containment vessels (Figure A-1). The 9975 shipping package design, performance, and analysis for safe transport of radioactive material are described in the Safety Analysis Report for Packaging (SARP) [1]. Celotex[®] fiberboard provides three safety functions: thermal insulation to limit internal temperature during a fire, criticality control, and resistance to package crushing [2]. The fiberboard material must retain its dimensions and density within certain ranges to provide the required impact resistance, criticality control, and fire resistance. The SRS Surveillance Program monitors material performance to establish a basis for service life and to ensure the continued integrity of 9975 packages [3-4].

Fiberboard samples, taken from multiple fiberboard assemblies fabricated from cane and softwood fiberboard, have been conditioning in elevated temperature environments since 2005. The samples are periodically examined to monitor thermal, mechanical, and physical properties, and assess degradation trends [5]. Fiberboard properties of interest that are evaluated to demonstrate acceptable long-term performance include dimensional stability, density, compressive strength, thermal conductivity, and specific heat capacity. Duplicate samples from multiple package sources have been tested to identify the range of variability in fiberboard properties and degradation rates.

Baseline and long-term testing of fiberboard material properties have been reported previously; reference 6 summarized experimental results of cane and softwood fiberboard through June 2021 and presented degradation models for the measured properties. This report presents the cumulative data collected through June 2022 and the corresponding updated aging models.

2.0 Experimental Procedure

2.1 Sample Sources and Conditioning Environment

Fiberboard samples were taken from cane and softwood source packages at various times after 2005 and are described in more detail in Appendix A. Samples were conditioned in ovens to provide nominally dry environments and in environmental chambers at controlled relative humidity (RH). Samples were aged in chambers at 125, 185, 215, and 250 °F and in environmental chambers at 125 °F + 70 % RH, 160 °F + 50 % RH, 185 °F + 30 % RH, and 185 °F + 70 % RH. Table 1 summarizes the maximum conditioning times for each environment through June 2022. Experimental activities and analysis are documented in an electronic laboratory notebook [7].

2.2 Sample Examination

Compression tests: The compressive behavior of fiberboard samples (nominally 2 x 2 x 2 inches) was tested using an Instron compression tester at a crosshead speed of 1.9 inch/minute. The compression samples are tested in either the parallel or perpendicular orientation where the load is applied parallel or perpendicular to the fiberboard layers, respectively. The samples are compressed until a limit is reached, either a maximum strain (85%) or a maximum load (20,000 pounds). Compression testing has been performed following conditioning for up to 11 years in some environments.

The ability of fiberboard samples to resist impact and crushing is evaluated using compression testing. Typical compression stress-strain curves of fiberboard samples conditioned at 185 and 250 °F are shown in Figure A-2. The integrated area under the stress-strain curve up to a strain of 40% provides a relative measure of the energy absorption capability of each sample. The 40% strain level is arbitrary but provides a consistent point for comparison.

Fiberboard samples are tested in both the parallel and perpendicular orientations relative to the fiberboard layers, but the latter provides data more relevant to the behavior of a 9975 package. For samples tested in the perpendicular orientation, the glue layers constrain lateral expansion which is similar to the constraint provided by the drum in the 9975 package. Samples tested in the parallel orientation without lateral constraint can split apart which can lead to underestimating the energy absorption capacity of fiberboard. Accordingly, only data collected in the perpendicular orientation will be used in modelling the degradation of energy absorption capability.

Thermal tests: Thermal testing is non-destructive and the same samples are examined at regular intervals. The ability of fiberboard samples (~7 x 7 x 1.5 inches) to transfer heat was tested using a LaserComp Fox 300 or 314 heat flow meter per ASTM C518-10. The thermal conductivity tests were conducted at mean temperatures of 25, 50, and 85 °C, and in the axial or radial direction. Heat flows through the assembly perpendicular to the fiberboard layers for axial samples and parallel to the fiberboard layers for radial samples.

The specific heat capacity of fiberboard samples (~1 inch diameter x 1.5 inch) was measured in accordance with ASTM C351-92b at mean test temperatures of 25 and 51 °C. Between three and five specific heat capacity samples are removed from the same fiberboard source and each sample can be examined several times at each test interval. Specific heat capacity data can show a significant degree of scatter from one trial to the next, and thus, results for all samples and trials are averaged for a given conditioning interval and temperature.

Physical tests: All samples (~2 x 2 x 2 inches) were dimensionally measured and weighed prior to conditioning in chambers and at regular intervals. In addition to the elevated temperature environments, samples were conditioned and examined at 15 and 50 °F, at ambient humidity and in a desiccated environment. For these low temperature environments, the ambient humidity is approximately 60% at 15 °F and 10% at 50 °F. No significant change in physical properties was noted in these low-temperature environments.

Table 1. Summary of maximum sample exposure times prior to testing for data through June 2022.

	Environment	Maximum exposure time (years) through June 2022				
		Thermal conductivity		Specific heat capacity	Compressive strength (⊥)	Physical properties
		Axial	Radial			
Cane	250 °F	4.9	4.9	5.0	4.8	5.3
	215 °F	15.6	15.6	—	7.4	16.0
	185 °F	16.6	16.6	16.6	8.7	16.2
	185 °F 30% RH	12.6	12.0	13.2	7.2	13.0
	185 °F 70% RH	0.4	0.4	0.4	1.2	1.3
	160 °F 50% RH	10.7	10.7	9.2	5.8	11.0
	125 °F	3.4	15.5	16.5	11.4	15.3
	125 °F 70% RH	10.6	10.6	0.3	6.7	10.8
Softwood	250 °F	3.7	4.9	4.4	4.8	4.0
	215 °F	13.2	13.2	—	8.5	13.3
	185 °F	7.1	7.1	—	7.1	13.5
	185 °F 30% RH	9.0	9.0	11.4	7.7	11.8
	185 °F 70% RH	1.4	0.9	—	0.8	1.4
	160 °F 50% RH	10.2	9.6	—	6.8	10.3
	125 °F	7.9	7.9	—	2.8	7.9
	125 °F 70% RH	10.6	10.6	—	6.6	10.8

2.3 Development of Aging Models

Fiberboard is composed primarily of three polymeric compounds: cellulose, hemicellulose, and lignin [8]. The literature indicates the degradation of cellulose, hemicellulose, and lignin occur at different rates with different chemical reactions, and cellulose will predominantly influence thermal degradation of fiberboard. Data for some properties, such as weight loss at 250 °F, show a varying degradation rate. The initial degradation rate reflects primarily the behavior of the compound that is degrading fastest and will be used in the aging model to enable a fair comparison of degradation rates across different aging environments. For samples in milder environments that display only one degradation regime, all of the data from these environments can be considered. The degradation models are applicable for fiberboard that maintain degradation behavior within this initial degradation regime and are below the temperature threshold of 185 °F. It is expected that thermo-oxidative degradation of fiberboard within this regime follows Arrhenius behavior where the degradation mechanism(s) do not change with temperature and can be described by the equation,

$$\text{rate constant} = Ae^{\frac{-Ea}{RT}}$$

where A is the Arrhenius constant, Ea is the activation energy, R is the ideal gas constant, and T is the absolute temperature.

The method for developing the aging models is described in detail in previous reports [9-11] and in the Appendix. In summary, data are normalized to the first conditioned value to compare data from multiple samples. All samples from a given environment are then averaged to better represent the bulk behavior of the fiberboard assembly. For physical properties and thermal conductivity, the degradation rate is calculated for each sample, and then, the rates for each sample within the environment are averaged. For compression test results, a single degradation rate is fit to all the samples from a given environment. A model has not been developed for specific heat capacity due to the large scatter in the data and small degradation rates observed.

Curves are fit to the degradation rate vs. reciprocal temperature and degradation rate vs. relative humidity plots for each property. Then, degradation rates are calculated using interpolations as a function of temperature (between 125 and 185 °F) and relative humidity (between 10 to 70% RH) to develop aging models for each fiberboard property. The aging models are applicable only within the initial degradation regime. Specific data correlations and curve fits used to develop each aging model are shown in the Appendix.

2.4 Quality Assurance

Requirements for the tasks covered in this report are established in reference 5 and manual 1Q 2-7. Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

To date, fourteen 9975 packages have been removed from KAC for destructive examination (DE) after being in storage for periods ranging from ~5 months to 16 years. The internal heat load of these packages ranged from 3 to 16.5 watts. Fiberboard degradation was evident in only one of these packages, which was in storage for 9.6 years with 16.5 watts internal heat load [12]. The remaining DE packages, with heat loads below 15 watts, indicate the storage environment is sufficiently mild to preclude significant fiberboard degradation over this period for most packages with low heat loads. Laboratory data and aging models supported increasing the approved storage life for 9975 packages with 3013 or non-3013 containers in KAC from 15 to 20 years [13-18], and then later, 9975 packages with 3013 containers from 20 to 40 years [19-

21]. Laboratory testing of fiberboard to analyze aging behavior and performance continues to predict service life of 9975 packages and support extending storage life.

The experimental results from evaluating the physical, thermal, and mechanical properties of fiberboard samples after extended conditioning in various environments are shown in Figure A-3 to Figure A-9. The figures show the variation in fiberboard properties and degradation rates between duplicate fiberboard samples and samples taken from different sources. There are generally insufficient data from a single source package among all environments to develop a complete degradation model so available data from all sources are averaged to generate the aging models.

Several samples have been conditioned at ambient laboratory conditions and periodically dimensionally measured and weighed. These samples displayed no significant permanent change in physical properties. Additionally, fiberboard samples conditioned at 125 °F demonstrate very low degradation rates. Given these minor changes, it was concluded that the threshold for fiberboard degradation was at approximately 120 °F [9]. For packages in KAC with internal heat loads below ~10-12 watts, most of the fiberboard assembly should remain below this threshold temperature and display insignificant fiberboard degradation.

Fiberboard within a 9975 package will develop temperature and moisture gradients due to the internal heat load. Moisture will tend to migrate to the cooler regions of the fiberboard while the total moisture content will change very slowly, if at all; any moisture originally in the fiberboard assembly will likely remain in the package for a long time. Laboratory tests have characterized the humidity profiles within packages with internal heat loads to demonstrate the range of environments that might exist within a package for a given moisture level and heat load [22-23]. A wide range of potential moisture conditions are possible and correspondingly, a range of fiberboard degradation trends. The actual moisture content of most packages is unknown.

In laboratory testing of fiberboard samples, there can be reversible property changes due to adjustments of moisture content in the conditioning environment and irreversible property changes due to degradation. Reversible changes due to changes in moisture content include thermal, physical, and mechanical properties. As moisture content decreases, thermal conductivity, specific heat capacity, weight, and dimensions of fiberboard samples all decrease. As moisture content increases, the energy absorption from compression tests in the perpendicular orientation decreases. Table A-1 in the Appendix summarizes the short-term physical property changes observed in the various environments. The weight changes are generally consistent with an initial moisture content of up to 10 wt. %.

In addition to short-term moisture effects, longer term changes in fiberboard properties may occur due to degradation. As the fiberboard degrades at elevated temperatures, water is released as a byproduct as well as other compounds from slow pyrolysis at temperatures as low as 203 °F [8]. For example, samples conditioned at 250 °F initially lose 8-10 wt. % due to moisture loss and then an additional 15-20 wt. % per year. Fiberboard samples conditioned at 250 °F darken and become more brittle (less fibrous and more particulate-like) with aging time. The aging models that are discussed below do not include the short-term effect of initial moisture change and involve only long-term degradation effects.

Aging models have been constructed based on the observed changes in several fiberboard properties and interpolating the degradation rates to other temperatures and relative humidity. The method for developing the models is described in detail in previous reports and in the Appendix [9-11]. The data correlation and curve fits for each fiberboard property used to develop the aging models are shown in Table A-2, Table A-3, Figure A-11, and Figure A-12. The models are based on the average behavior of all cane and softwood samples and do not reflect any variation among packages or duplicate samples. The aging models are shown in Figure 1 - Figure 7 for weight, height, length/width, density, thermal conductivity (axial and radial

orientations) and energy absorption (perpendicular orientation). In general, the degradation rate increases with increasing temperature and humidity.

Previous testing of humidity in 9975 packages with internal heat loads up to 19 watts determined 42 g/m^3 as an upper bound absolute humidity value for conforming packages (*e.g.*, no mold in fiberboard) [22-23]. As relative humidity is dependent upon temperature, at 42 g/m^3 , the relative humidity will vary from 53% at 120 °F to 26% at 150 °F. Thermal and structural calculations that supported extending the service life of 9975 packages to 20 years and 40 years storage assumed a maximum fiberboard temperature of 146 °F and 150 °F, respectively [15-17, 21]. The calculations assumed density, dimensional, and thermal properties were reduced at a rate of 0.5% per year for 20 year and 40 year evaluations. Conservatism in the 20 year structural analysis used a degradation rate of 1.6% per year for temperatures up to 145 °F for fiberboard strength, while the 40 year structural analysis used a rate of 1.25% per year. By comparing the dashed bounding absolute humidity line (42 g/m^3) in each model in Figure 1 - Figure 7 with the degradation rate contours, the following statements can be made about the behavior of fiberboard maintained below the 42 g/m^3 line:

- The degradation rates for fiberboard dimensions and density are below ~0.4% per year for all temperatures up to 160 °F.
- The degradation rate for radial thermal conductivity is less than 0.5% per year for all temperatures up to 160 °F.
- The degradation rate for axial thermal conductivity is less than 0.5% per year for all temperatures up to 130 °F and between 0.5% and 0.6% per year between 130 and 160 °F.
- The degradation rate for energy absorption is ~1% per year between 130 and 145 °F and less than 2% per year between 145 and 160 °F.

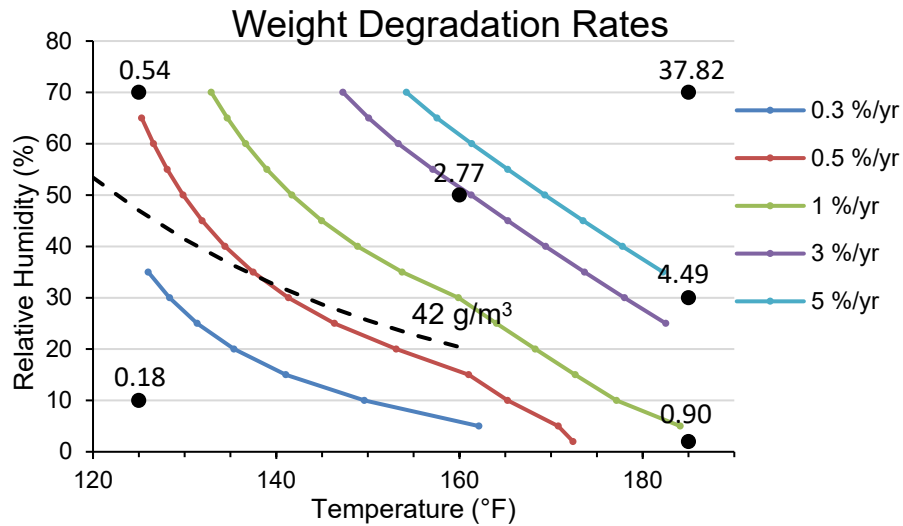
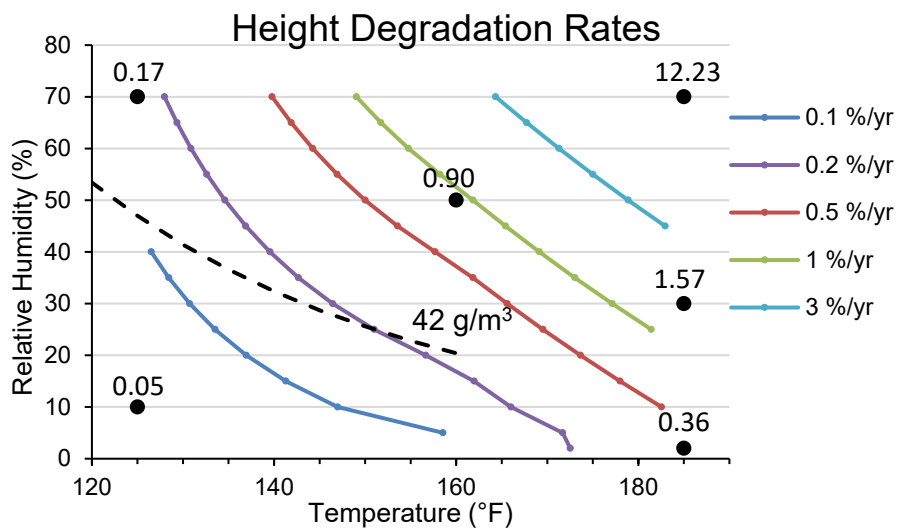
The degradation rates associated with the bounding absolute humidity of 42 g/m^3 and a bounding temperature of 160 °F are within that assumed for recent thermal and structural calculations for fiberboard dimensions, density, and radial thermal conductivity (*e.g.*, degradation rates $\leq 0.5\%$ per year). The aging model for axial thermal conductivity estimates the degradation rate slightly exceeds 0.5% per year between 130 and 160 °F. Additional data will continue to be collected to permit future refinements to the models and assumptions.

If it is assumed that fiberboard degradation follows Arrhenius behavior, like other polymeric materials, then the temperature dependence of fiberboard degradation can be described by the activation energy. The average degradation rates for each property are plotted vs. reciprocal temperature in Figure A-11 and Figure A-12, and the exponential coefficients are used to calculate the activation energies. The calculated activation energy for each fiberboard property in the dry oven environments are presented in Table 2. From weight loss data, the calculated activation energy for fiberboard samples aging in dry environments is 90.7 kJ/mol. This is in reasonable agreement with literature values of 109-151 kJ/mol for the activation energy of cellulose, a primary component of softwood and cane fiberboard [24-26]. SRNL previously reported the calculated activation energy was approximately 38 kJ/mol for fiberboard degradation based upon weight measurements at absolute humidity of 40 g/m^3 [9]. This is consistent with literature trends for wood products to have lower activation energy in humid conditions [26]. As lower activation energy means faster rate when comparing the same reaction, the rate of thermal degradation for fiberboard samples is higher in humid than in dry conditions.

There may be sources of degradation to the fiberboard not accounted in the laboratory testing. For example, a limited number of 9975 packages have been removed from service and found to contain mold or drugstore beetles. To date, beetles [27] and mold have been observed in three and twelve packages, respectively. The specific impact of beetles or mold on fiberboard properties are not addressed in this report.

Table 2. Calculated activation energy from the degradation models for dry oven environments.

Fiberboard property	Activation energy (kJ/mol)
Energy absorption	83.5
Weight	90.7
Height	90.2
Length / width	78.1
Radial thermal conductivity	88.6
Axial thermal conductivity	79.1

**Figure 1.** Fiberboard weight loss model with lines representing contours of equal rate of weight loss. Numerical values are the average degradation rates (%/year) of aged samples. The dashed line indicates those environments for which the absolute humidity is 42 g/m^3 .**Figure 2.** Fiberboard height loss model with lines representing contours of equal rate of height loss. Numerical values are the average degradation rates (%/year) of aged samples.

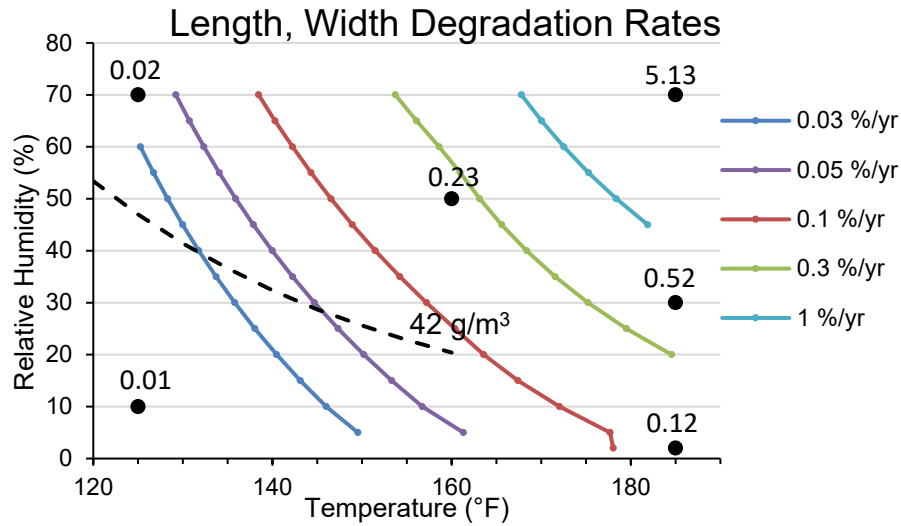


Figure 3. Fiberboard length/ width loss model with lines representing contours of equal rate of length/ width loss. Numerical values are the average degradation rates (%/year) of aged samples.

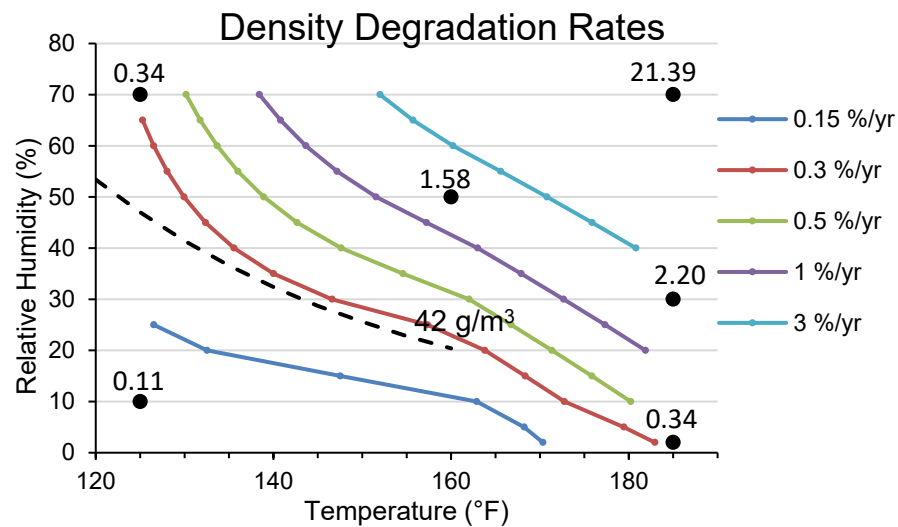


Figure 4. Fiberboard density loss model with lines representing contours of equal rate of density loss. Numerical values are the average degradation rates (%/year) of aged samples.

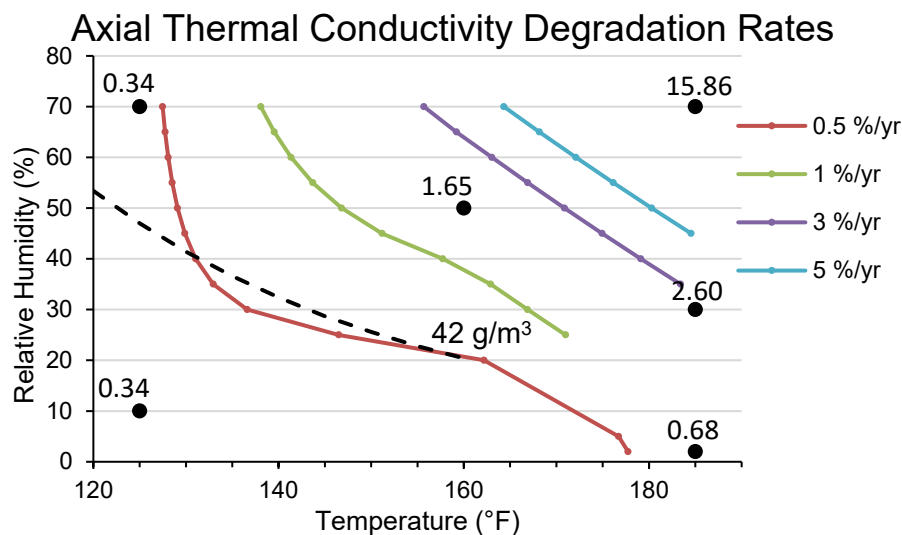


Figure 5. Fiberboard thermal conductivity model with lines representing contours of equal rate of thermal conductivity decrease in the axial orientation. Numerical values are the average degradation rates (%/year) of aged samples.

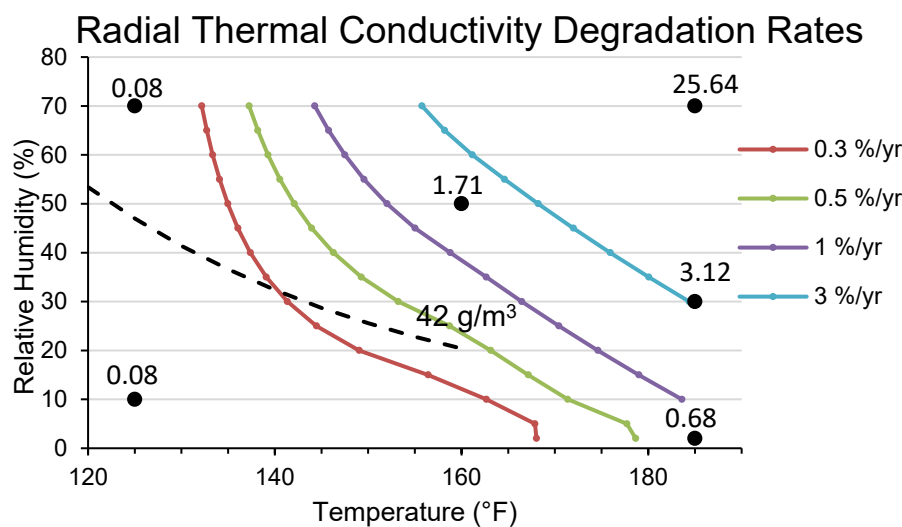


Figure 6. Fiberboard thermal conductivity model with lines representing contours of equal rate of thermal conductivity decrease in the radial orientation. Numerical values are the average degradation rates (%/year) of aged samples.

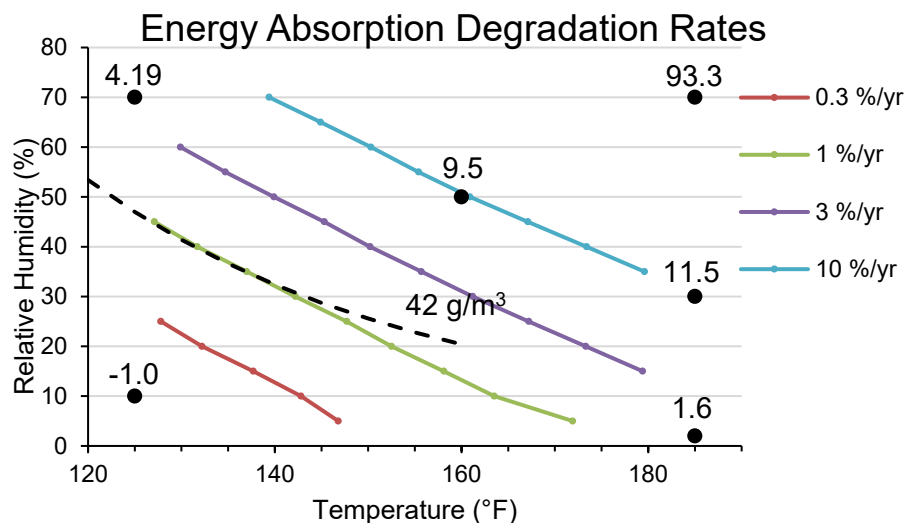


Figure 7. Fiberboard energy absorption model with lines representing contours of equal rate of energy absorption loss for compression samples tested in the perpendicular orientation. Numerical values are the average degradation rates (%/year) of aged samples.

4.0 Conclusions

The thermal, mechanical, and physical properties of cane and softwood fiberboard samples have been evaluated following conditioning in elevated temperature and/or humidity environments for up to 17 years. Most of the aging environments are bounding to the conditions expected within the 9975 shipping package during storage in KAC. Models have been developed from these data to provide estimates of degradation rate under potential storage conditions for several fiberboard properties, including thermal conductivity, energy absorption, weight, dimensions, and density. Generally, the degradation rates for fiberboard increased with increasing temperature and humidity. The degradation rates associated with the bounding absolute humidity of 42 g/m^3 and a bounding temperature of 160°F are $\leq 0.5\%$ per year for fiberboard dimensions, density, and radial thermal conductivity. The axial thermal conductivity degradation rate slightly exceeds 0.5% per year between 130 and 160°F . The calculated activation energy, using sample weight changes in dry environments, for fiberboard degradation is approximately 90.7 kJ/mol and is consistent with literature values for wood products. The models support the currently approved 20 year service life for 9975 packages with non-3013 containers and 40 year service life for 9975 packages with 3013 containers. Additional data continue to be collected to refine aging models and service life predictions.

Some of the degradation rates and model predictions presented in this report are extreme and do not represent the behavior of a typical package in KAC. The internal heat load and temperature profiles within many packages in storage are such as to produce milder conditions in storage than in any of the aging environments. Many conforming packages with low internal heat loads are expected to experience no or little degradation; only one out of fourteen destructively examined 9975 package showed evidence of fiberboard degradation. Nevertheless, the possibility of accelerated degradation to a limited number of packages, whether from high heat load, elevated moisture levels, or other conditions, should be recognized. These packages will experience degradation in service and may not perform their required safety functions beyond 40 years.

The assumptions and inputs behind the predictions in this report should be well understood before attempting to estimate an actual service life in KAC. A limited number of 9975 packages have been found with non-conforming conditions (e.g., mold in fiberboard). The analysis and predictions of this report

should not be applied to non-conforming packages. Additional efforts would be needed to address the integrity of the fiberboard in such packages.

5.0 References

1. "Safety Analysis Report for Packaging Model 9975", Savannah River Nuclear Solutions, S-SARP-G-00003, Rev. 4, 2015.
2. "K-Area Complex Documented Safety Analysis", Savannah River Nuclear Solutions, WSRC-SA-2002-00005, Rev. 16, 2021.
3. Kiflu, B. B., "Summary and Matrix: 9975 Shipping Package Qualification Program for Extended Storage of Plutonium in the K-Area Complex", Savannah River Nuclear Solutions, SRNS-TR-2008-00290, Rev. 2, 2016.
4. Escobar, A. J., "Savannah River Site Surveillance Program for the Storage of 9975/3013 Plutonium Packages in KAC", Savannah River Nuclear Solutions, WSRC-TR-2001-00286, Rev. 10, 2021.
5. "Task Technical and Quality Assurance Plan for Characterization and Surveillance of Model 9975 Shipping Package O-Rings and Fiberboard Materials", SRNL-TR-2014-00057, 2014.
6. Truong, T. T.; Lowe, Z., "2021 Status report - Fiberboard properties and degradation rates for storage of 9975 shipping package in KAC", Savannah River National Laboratory, SRNL-STI-2021-00406, 2021.
7. Truong, T. T., 9975 Shipping Package Testing and Evaluation, 2020.
8. Browne, F. L., "Theories of the combustion of wood and its control: a survey of the literature", Forest Products Laboratory, FPL-2136, 1963.
9. Daugherty, W. L.; Truong, T. T., "Status report - Fiberboard properties and degradation rates for storage of the 9975 shipping package in KAC", Savannah River National Laboratory, SRNL-STI-2018-00127, 2018.
10. Daugherty, W. L., "Status Report - Cane Fiberboard Properties and Degradation Rates for Storage of the 9975 Shipping Packag in KAC", Savannah River National Laboratory, SRNL-STI-2015-00610, 2015.
11. Daugherty, W. L., "Status Report - Softwood Fiberboard Properties and Degradation Rates for Storage of the 9975 Shipping Package in KAC", Savannah River National Laboratory, SRNL-STI-2015-00611, 2015.
12. Daugherty, W. L., "Destructive examination of shipping package 9975-02644", Savannah River National Laboratory, SRNL-STI-2017-00666, 2017.
13. Grimm, R. J., "9975 Shipping Package/ 3013 Container 20 Year Life Extension Summary", Savannah River Nuclear Solutions, G-ESR-K-00204, 2017.
14. Escobar, A. J.; Hensel, S. J., "9975 Shipping Package/non-3013 Container 20 Year Life Extension Summary", Savannah River Nuclear Solutions, G-ESR-K-00231, 2019.
15. Kiflu, B. B., "The Initial and 20-year Service Thermal Performances of the 9975 Shipping Packages due to Fire-Drop-Smoldering Accidents in KAC", M-CLC-K-00788, 2017.
16. Kiflu, B. B., "The Initial and 20-year Service Thermal Performances of the 9975 Shipping Packages due to Fire Accident in KAC Facility", M-CLC-K-00789, 2017.
17. Johnson, J., "Dynamic Analysis of 30-ft Drop for 9975 Package in Storage Conditions", M-CLC-K-00786, 2017.
18. McKeel, C., "Structural Analysis of the 9975 Package for a Facility Condition Forklift Accident with 20 year Aged Package Conditions", M-CLC-K-00787, 2017.

19. O'Grady, A. J., "9975 Shipping Package/3013 40 Year Life Extension Summary", Savannah River Nuclear Solutions, G-ESR-K-00253, 2022.
20. Tamburello, D. A., "Thermal Analysis of 40-Year 9975 Package During Fire Accident", Savannah River National Laboratory, M-CLC-A-00629, 2018.
21. McKeel, C., "Structural Analysis of the 9975 Package for a Facility Condition Accidents with 40 year Aged Package Conditions", M-CLC-K-00821, 2020.
22. Daugherty, W. L., "Humidity Data for 9975 Shipping Packages with Cane Fiberboard", Savannah River National Laboratory, SRNL-STI-2016-00254, 2016.
23. Daugherty, W. L., "Humidity Data for 9975 Shipping Packages with Softwood Fiberboard", Savannah River National Laboratory, SRNL-STI-2017-00009, 2017.
24. Ramiah, M. V., Thermogravimetric and differential thermal analysis of cellulose, hemicellulose, and lignin. *Journal of Applied Polymer Science* **1970**, 14 (5), 1323-1337.
25. Shafizadeh, F., The Chemistry of Pyrolysis and Combustion. In *The Chemistry of Solid Wood*, American Chemical Society: 1984; Vol. 207, pp 489-529.
26. Stamm, A. J., Thermal Degradation of Wood and Cellulose. *Industrial & Engineering Chemistry* **1956**, 48 (3), 413-417.
27. Daugherty, W. L., "Examination of beetle-infested shipping package 9975-03996", Savannah River National Laboratory, SRNL-STI-2014-00431, 2014.

Appendix A. Supplemental Information

Fiberboard source packages:

Samples have been taken from the following sources and used in developing aging models:

- LD1 and LD2 - undamaged portions of two cane fiberboard lower assemblies from drop tested packages, which were in storage for ~10 years prior to this effort. The first samples began conditioning in 2005.
- MSC – undamaged portions of several cane fiberboard lower assemblies from drop tested packages, which were in storage for ~10 years prior to this effort. Traceability to specific assemblies was not maintained for these samples. The first samples began conditioning in 2005.
- 2234 – cane fiberboard lower assembly removed from package 9975-02234 following two year service in KAC and subsequent surveillance activities. The first samples began conditioning in 2006.
- New – remnant portions of a new cane fiberboard assembly (upper and lower) purchased in 2005 for a separate effort. The first samples began conditioning in 2006.
- SW – a new softwood fiberboard lower assembly provided by KAC. The first samples began conditioning in 2008.
- T4SW and T5SW – softwood fiberboard lower assembly from training packages T4 and T5. Samples began conditioning in 2014.
- 6100 – softwood fiberboard from package 9975-06100 following field surveillance and destructive examination. Samples began conditioning in 2014.

Samples from the following sources have been examined but were not considered in developing aging models due to limited sample size.

- KT2 – cane fiberboard lower assembly from an unused package following several (<5) years in storage. These samples began conditioning in 2006.
- 826 – cane fiberboard lower assembly removed from package 9975-00826 following three year service in KAC and subsequent surveillance activities. The first samples began conditioning in 2006.
- 826U, 600U – cane fiberboard upper assemblies removed from packages 9975-00826 and 9975-00600 following three and five year service in KAC, respectively, and subsequent surveillance activities. Samples began conditioning in 2009.

Table A-1. Change in physical properties during initial transition to aging environment

Environment	Approximate initial change in			
	Weight	Density	Height	Length, Width
250 °F	8 – 10% decr	3 – 6% decr	2 - 3% decr	0 - 2% decr
215 °F	7 – 9% decr	3 – 6% decr	0.5 - 3% decr	0 - 2% decr
185 °F	7 – 8% decr	4 – 5% decr	2 - 3% decr	< 1% (+ and -)
125 °F	5 – 6% decr	3 – 4% decr	1 - 2% decr	< 0.5% (+ and -)
185 °F, 70%RH	< 1% (+ and -)	2 – 6% decr	1 – 3% incr	< 1% (+ and -)
185 °F, 30%RH	4 – 5% decr	2 – 3% decr	1 - 2% decr	< 0.5% decr
160 °F, 50%RH	< 1% (+ and -)	3% decr – 2% incr	< 1% (+ and -)	< 0.5% decr – < 1% incr
125 °F, 70%RH	2% incr	0.5% decr – 2% incr	0 – 3% incr	1% decr – 2% incr

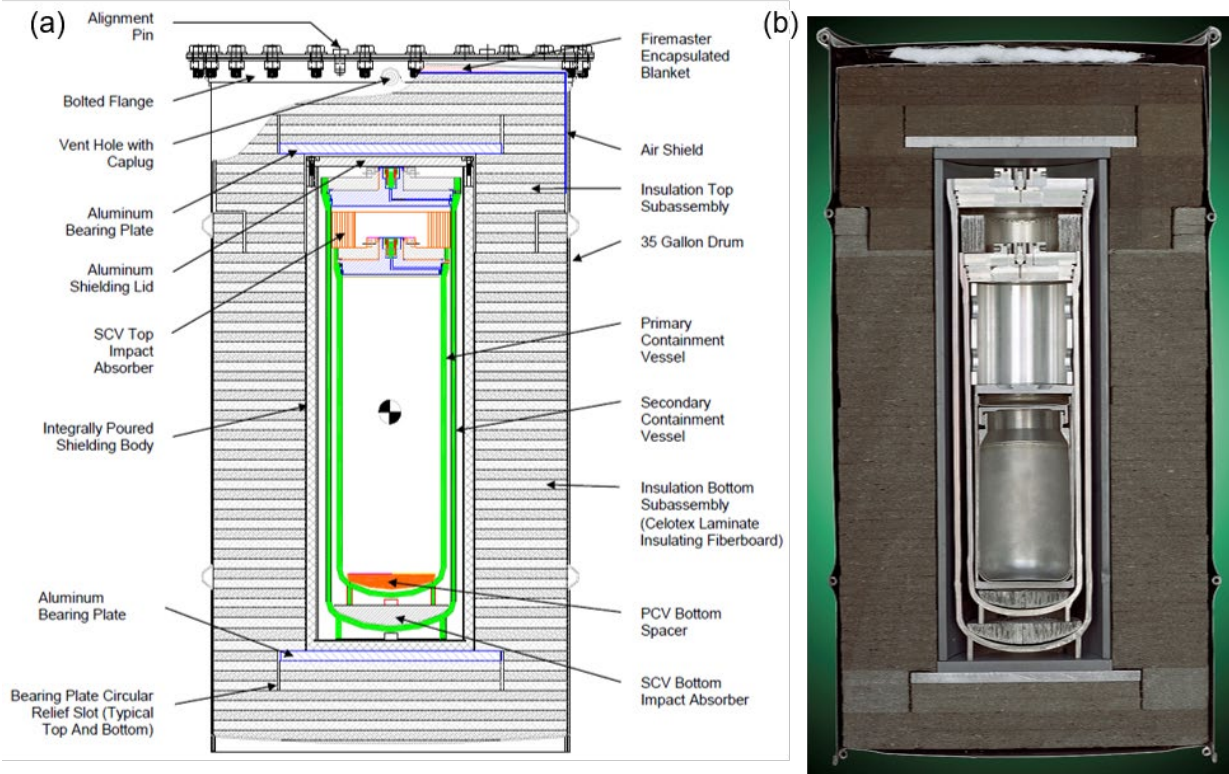


Figure A-1. (a) Labeled cross section and (b) picture of cross section of 9975 shipping package.

Steps to compile aging models for each fiberboard property:

1. Compile plots of fiberboard data normalized to their initial conditioned value for each sample (Figure A-4 - Figure A-9)
2. Determine the degradation rate for each sample and the average degradation rates for all samples
 - a. For varying degradation rates (changing degradation mechanisms), the data is restricted to the initial ~constant degradation rate
 - b. Compile the average degradation rate at each conditioning environment for each fiberboard property in Table A-2 and Table A-3
 - c. For length/width degradation rates, compile the average of both length and width degradation rates
3. For non-humid conditioning environments at 185, 215, 250 °F, fit an exponential curve to the degradation rate vs. reciprocal temperature for each fiberboard property (plots on the left in Figure A-11 and Figure A-12)
4. Fit an exponential curve to the degradation rate vs. relative humidity for each property at 125, 160, and 185 °F (plots on the right in Figure A-11 and Figure A-12)
5. Using the exponential equations determined from the plots of Figure A-11 and Figure A-12, extrapolate the expected degradation rate for each fiberboard property at 125, 160, and 185 °F for varying relative humidity values from 2 to 70 % RH
6. Using the degradation rates calculated from the previous step, fit an exponential curve between 125 and 160 °F, and between 160 and 185 °F for each RH.
7. Using the exponential equations from the previous steps, create an array of degradation rates for each RH between 2% and 70% and for each temperature between 125 and 185 °F.
8. Using the developed array of degradation rates as a function of temperature and relative humidity, plot the degradation rate at determined values (*e.g.*, 0.5% per year).

9. Connecting the degradation rates at determined values will become contour lines in aging models for each property (Figure 1 -Figure 7)

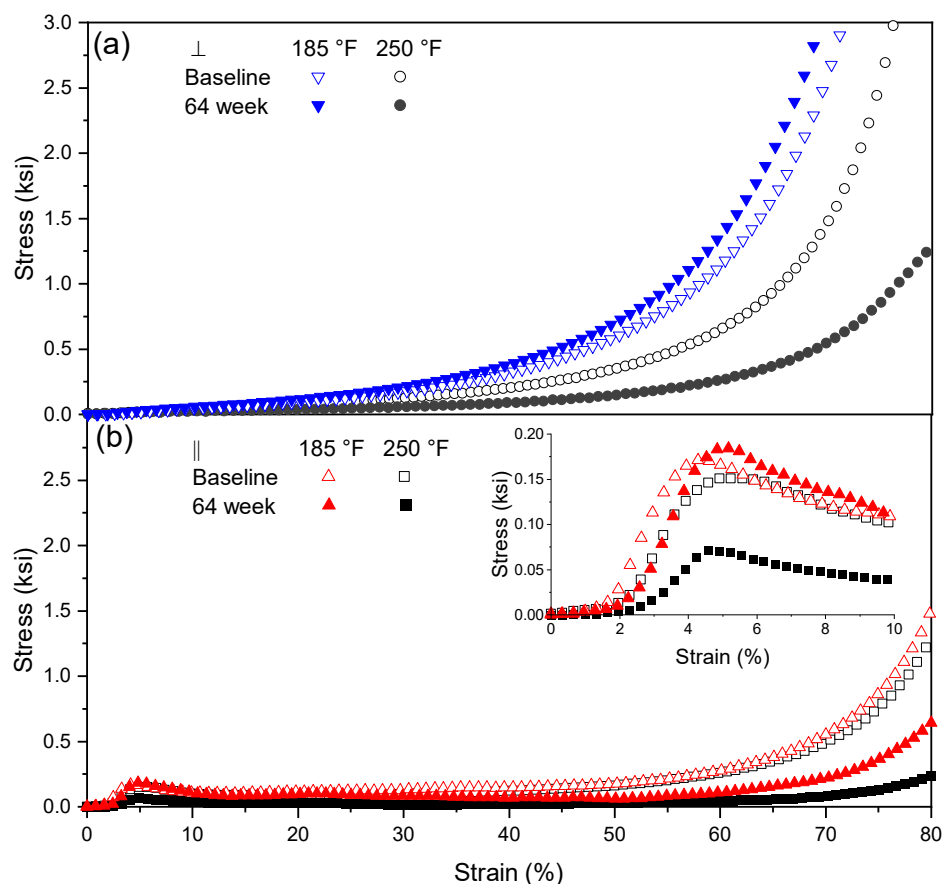


Figure A-2. Plots of compression curves for select fiberboard samples conditioned at 185 and 250 °F and compressed in the (a) perpendicular and (b) parallel orientation.

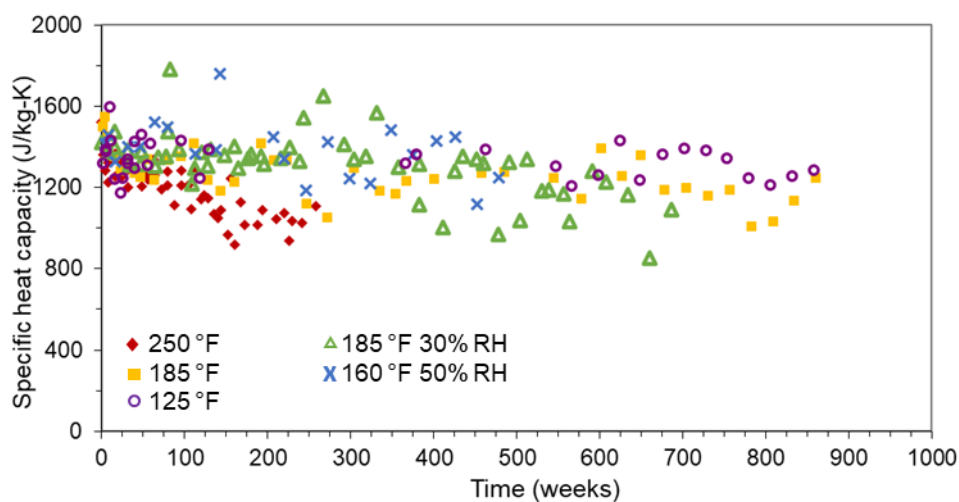


Figure A-3. Specific heat capacity data at a mean temperature of 52 °C for fiberboard samples aged in different environments.

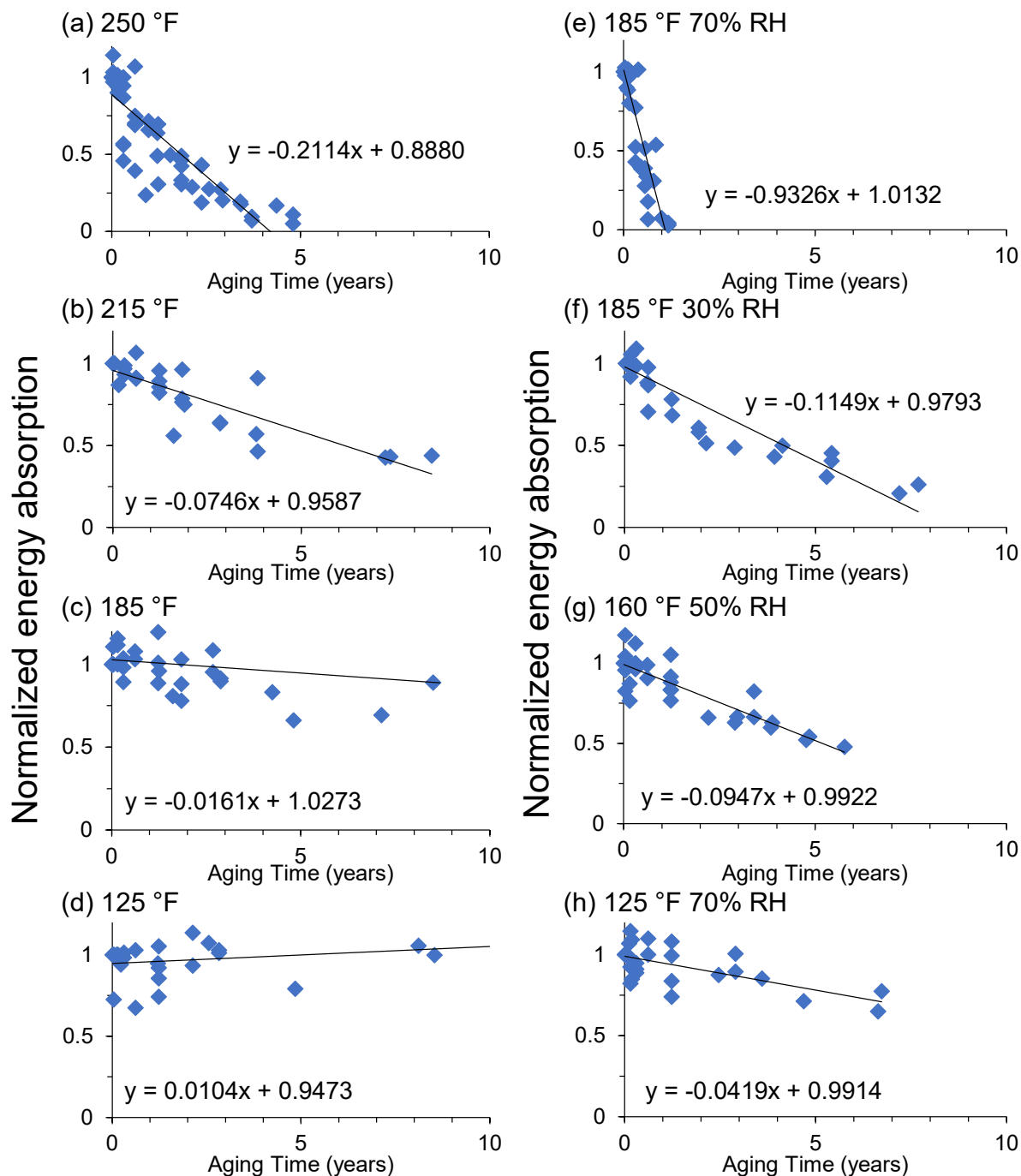


Figure A-4. Plots of energy absorption data from perpendicular orientation compression tests of fiberboard samples aged in different environments.

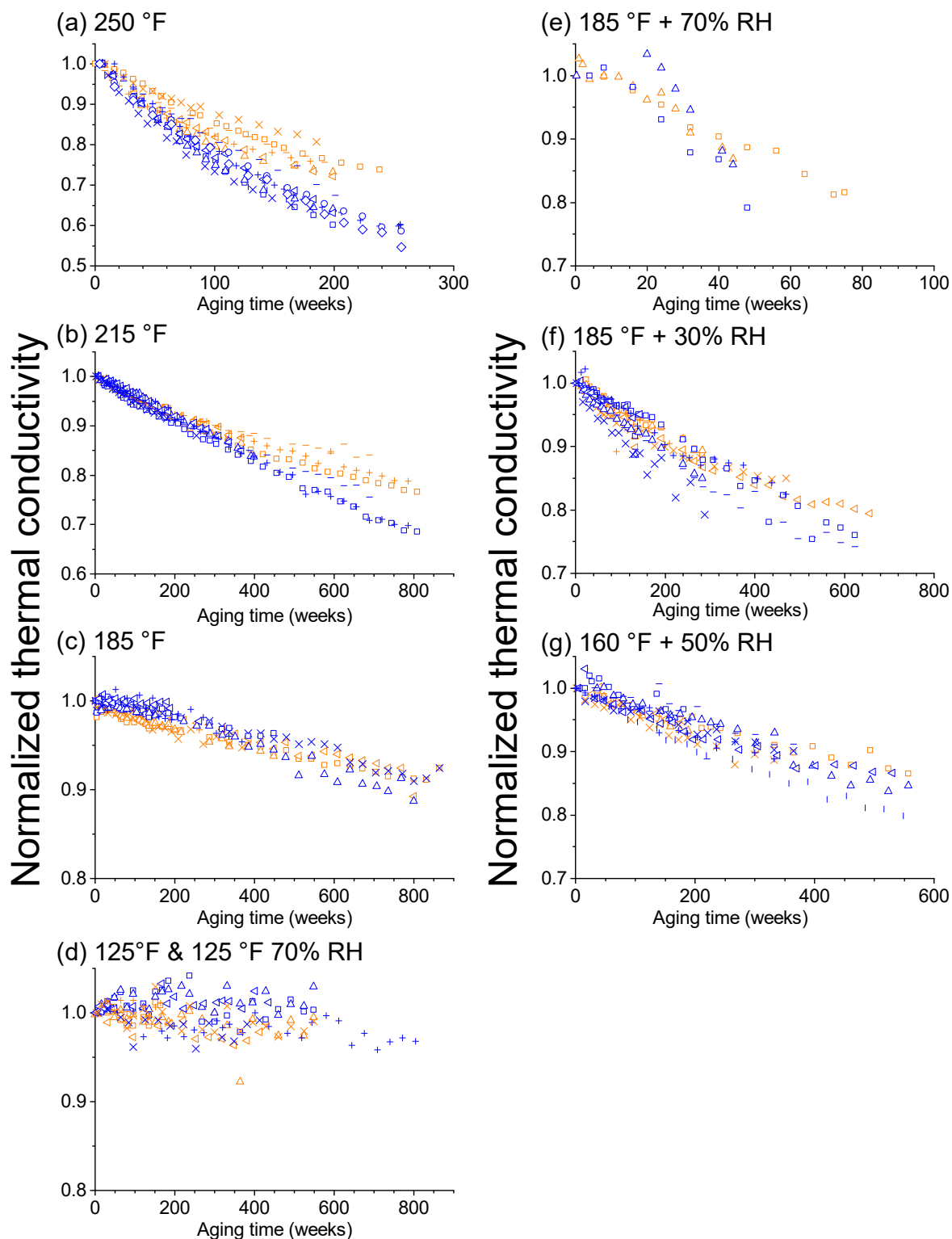


Figure A-5. Plots of thermal conductivity data measured at 25 °C mean temperature for fiberboard samples aged in different environments. Axial orientation samples are shown in orange, and radial orientation samples are shown in blue.

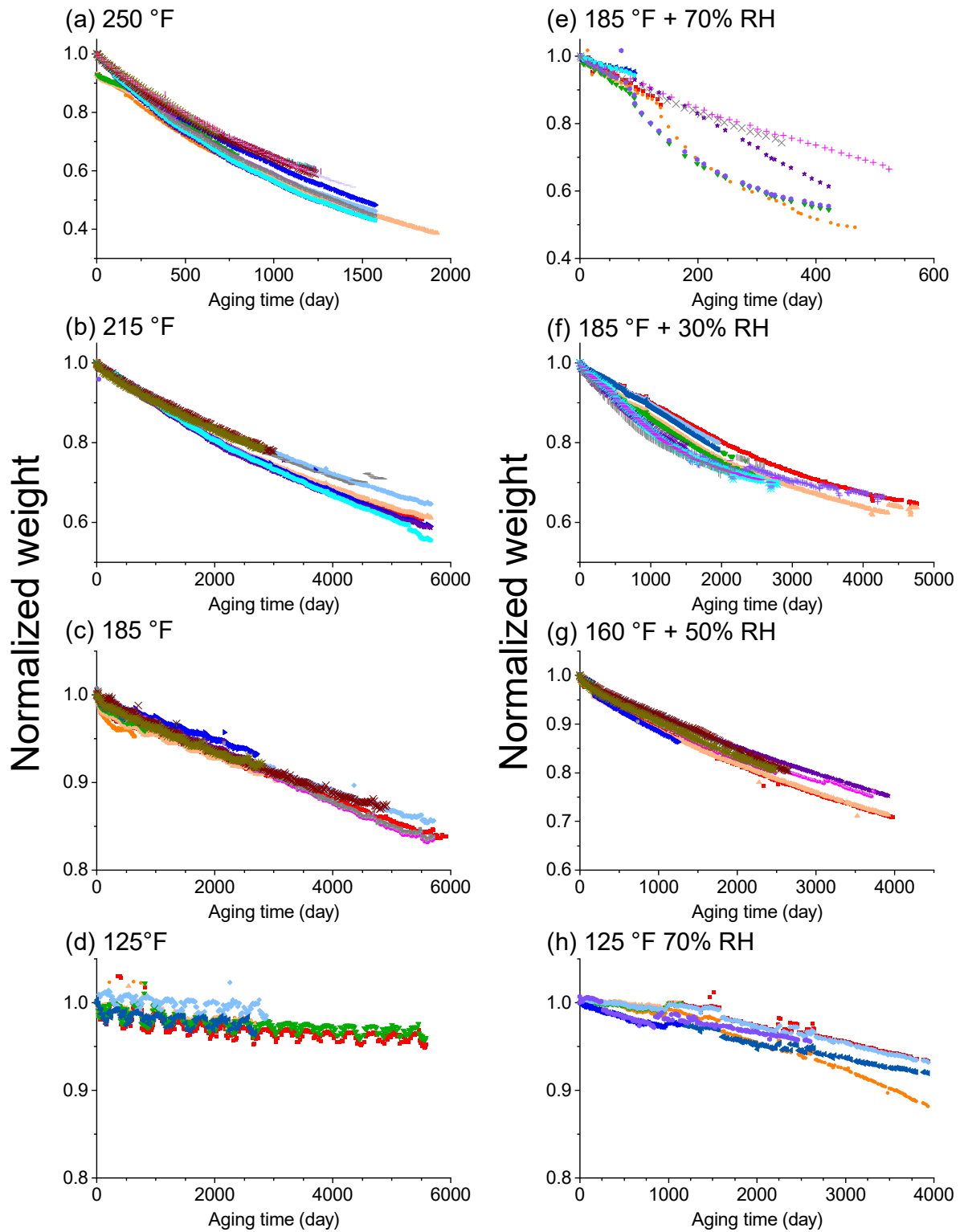


Figure A-6. Plots of weight data for fiberboard samples aged in different environments.

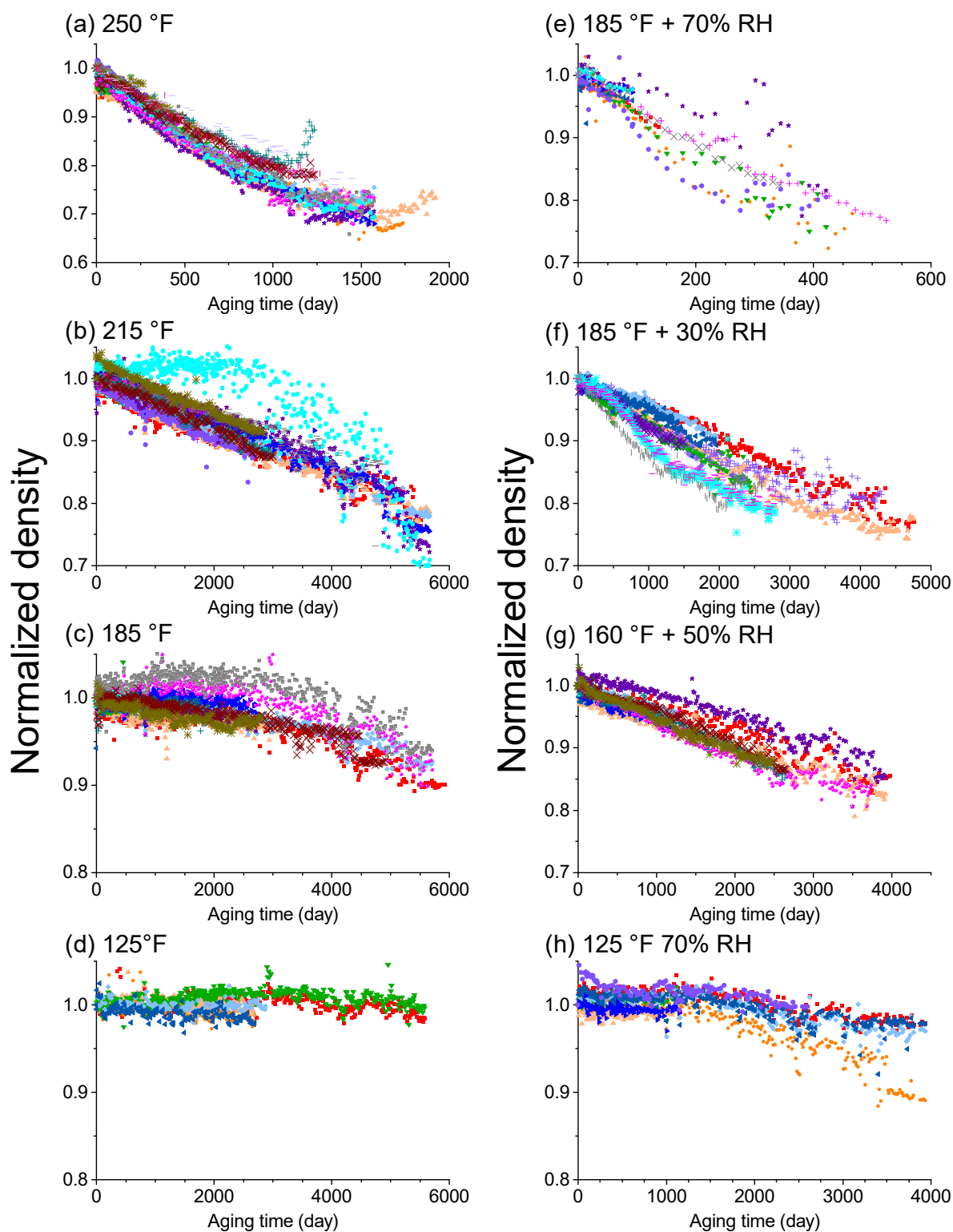


Figure A-7. Plots of density data for fiberboard samples aged in different environments.

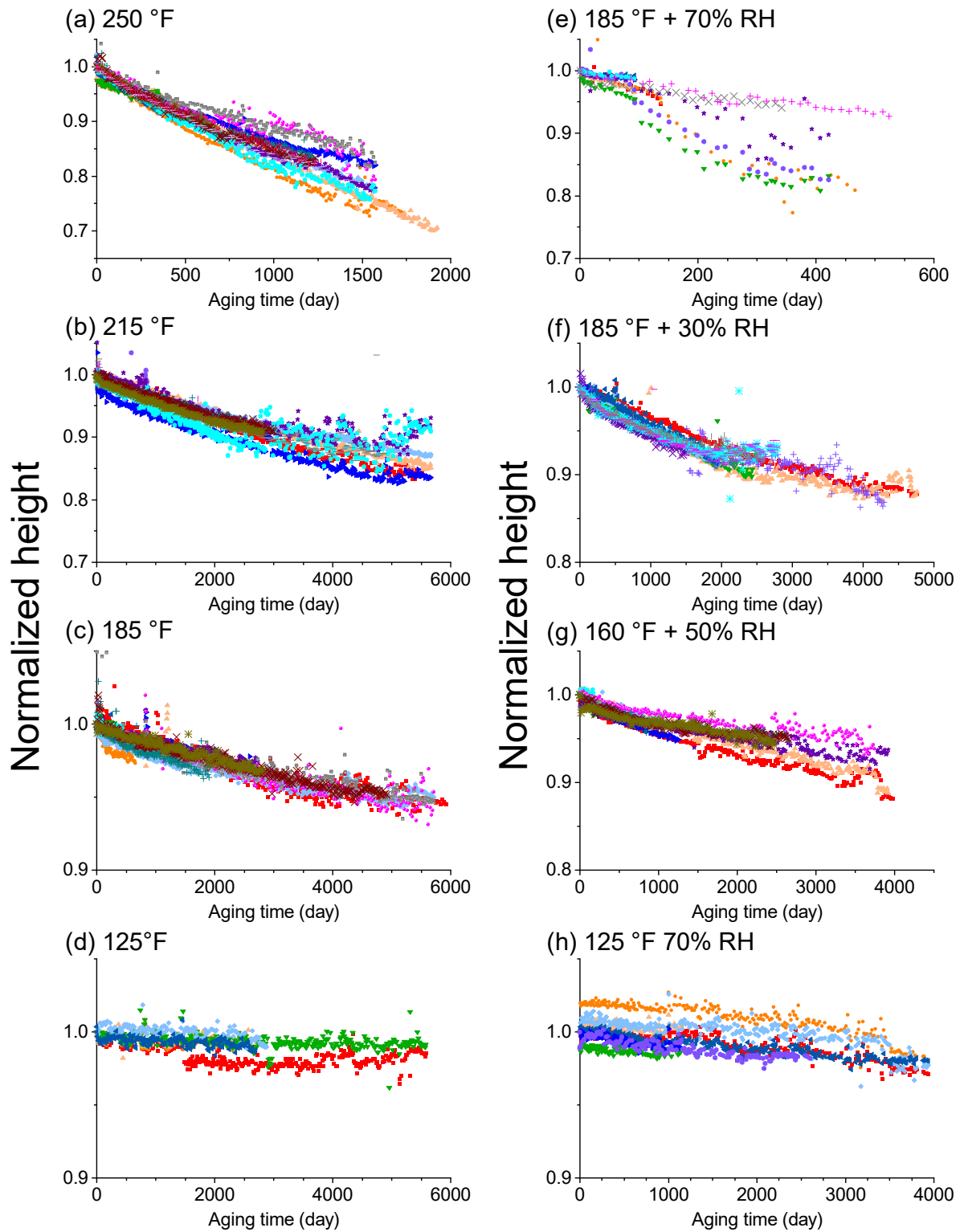


Figure A-8. Plots of height data for fiberboard samples aged in different environments.

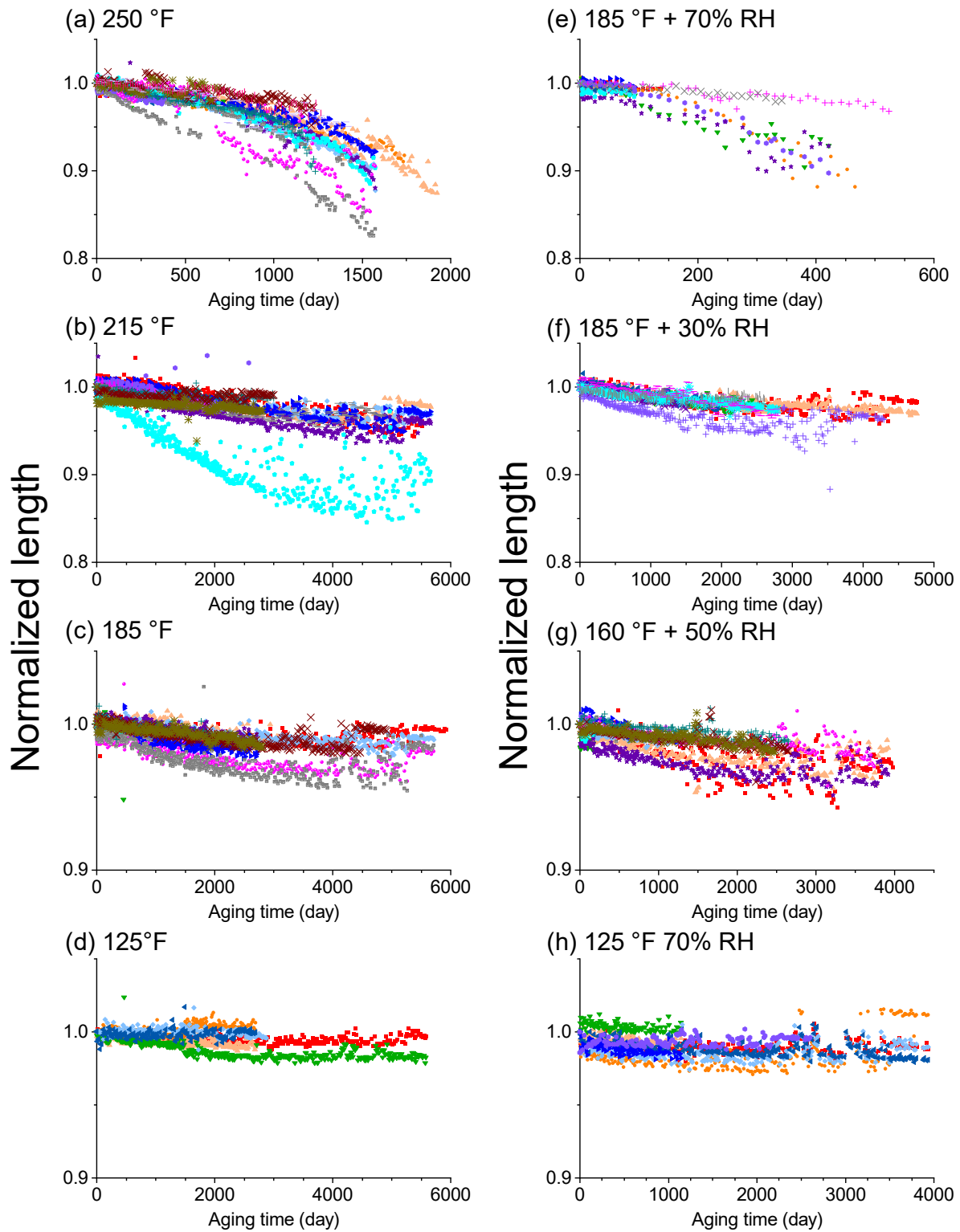


Figure A-9. Plots of length data for fiberboard samples aged in different environments.

Table A-2. Average degradation rates (%/year) for physical properties.

Environment	Weight	Density	Height	Length, Width
Control samples	-0.059	0.029	-0.027	-0.030
125 °F	-0.18	-0.11	-0.05	-0.01
125 °F 70% RH	-0.54	-0.34	-0.17	-0.02
160 °F 50% RH	-2.75	-1.57	-0.89	-0.23
185 °F	-0.96	-0.38	-0.38	-0.12
185 °F 30% RH	-4.86	-2.86	-1.55	-0.41
185 °F 70% RH	-36.54	-19.22	-12.26	-5.70
215 °F	-3.08	-1.28	-1.22	-0.41
250 °F	-15.60	-8.70	-6.02	-1.35

The rates for each aging environment have been adjusted by the control sample rates which have been aged at ambient conditions. When a sample displayed a change in degradation over time, only the initial rate is reflected in this table.

Table A-3. Average degradation rates (%/year) for thermal conductivity and energy absorption.

Environment	Thermal conductivity		Energy Absorption
	Radial orientation	Axial orientation	Perpendicular orientation
125 °F	-0.08	-0.34	1.04
125 °F 70% RH	-0.11	-0.10	-4.19
160 °F 50% RH	-1.72	-1.64	-9.47
185 °F	-0.74	-0.69	-1.61
185 °F 30% RH	-2.93	-2.87	-11.49
185 °F 70% RH	-26.42	-15.25	-93.30
215 °F	-2.13	-2.12	-7.46
250 °F	-11.24	-7.87	-21.44

When a sample displayed a change in degradation over time, only the initial rate is reflected in this table.

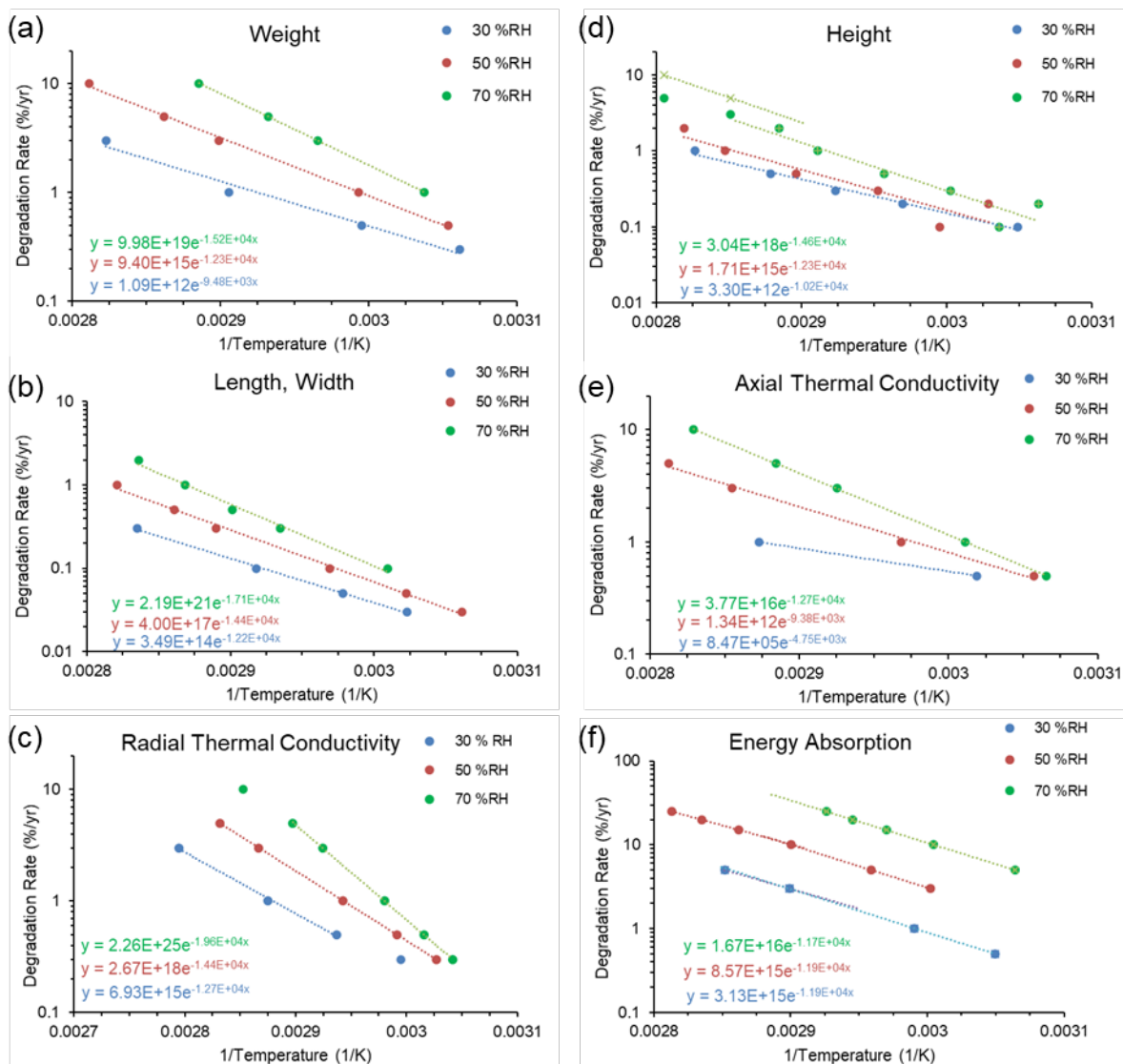


Figure A-10. Arrhenius plots of degradation rates for the identified properties at different temperatures and relative humidity.

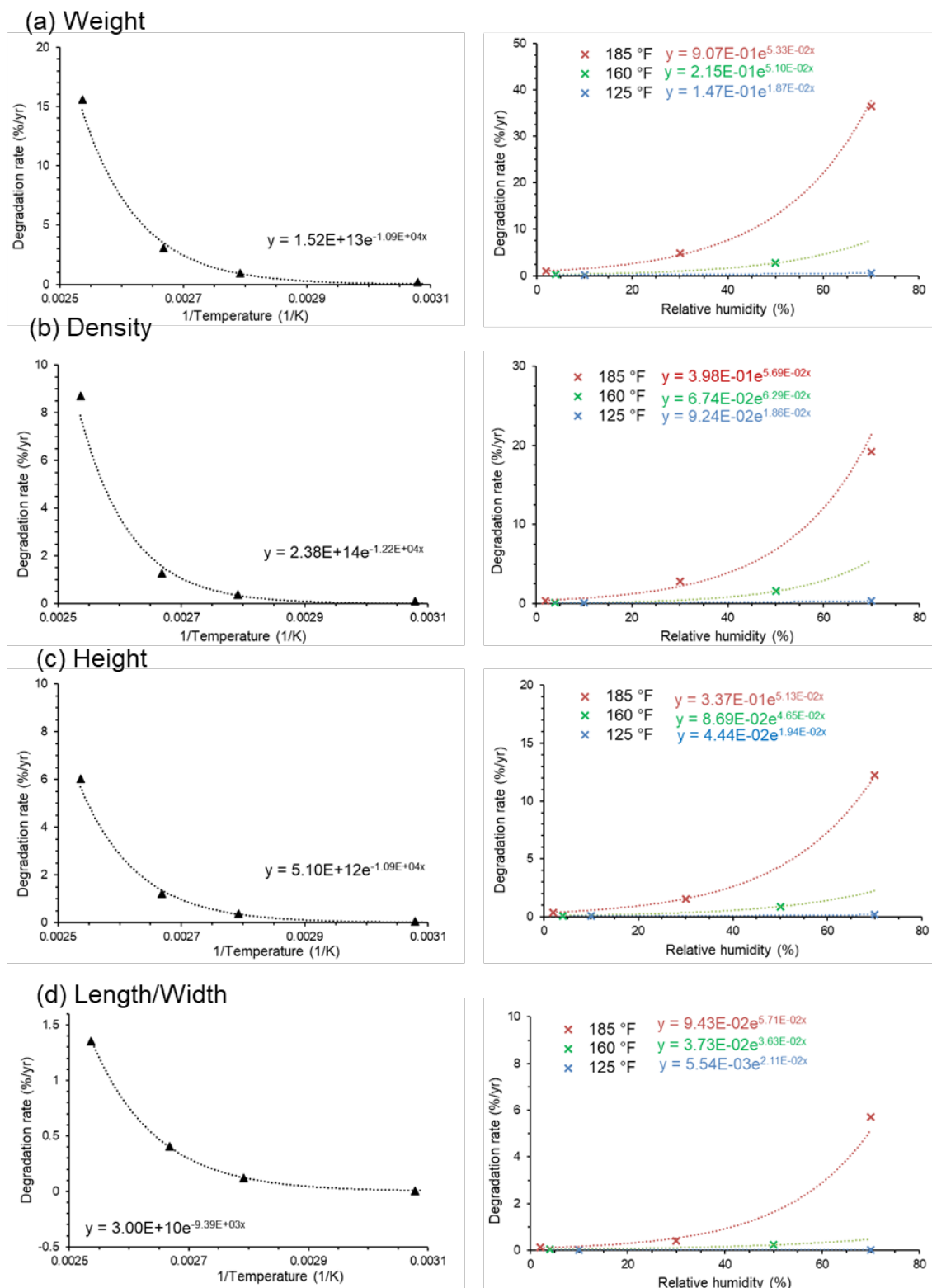
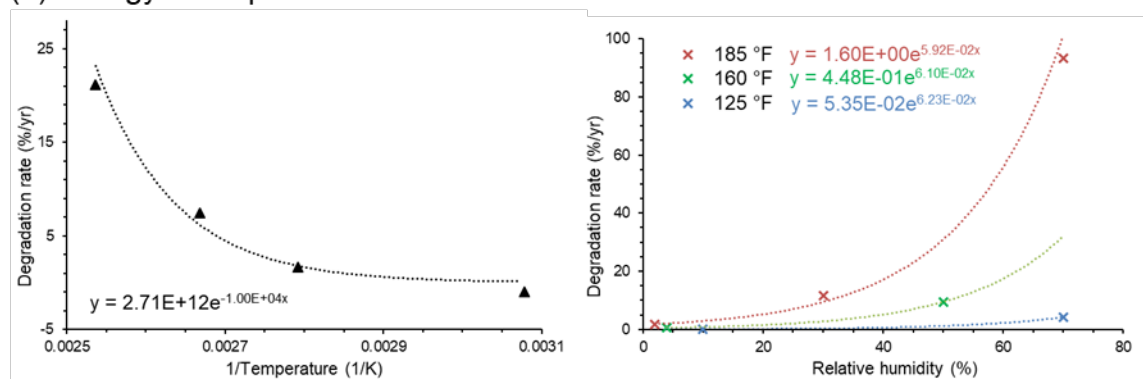
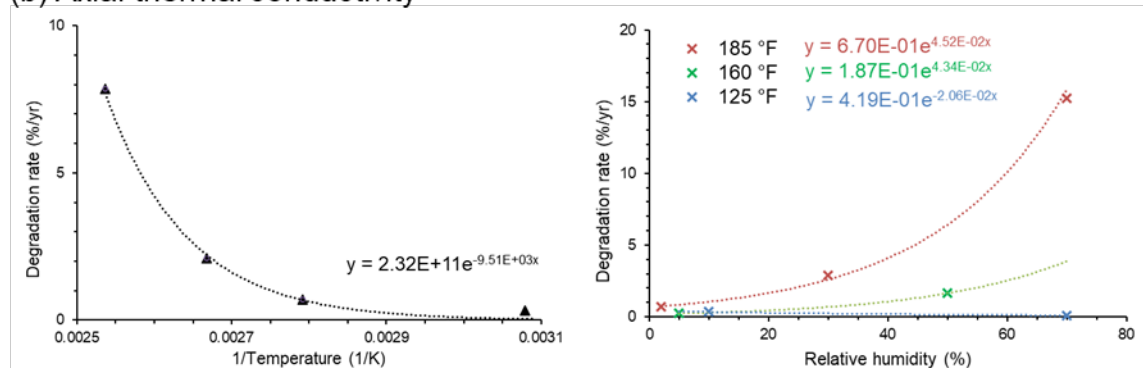


Figure A-11. Plots of degradation rate vs. reciprocal temperature (left) and vs. relative humidity (right) for the identified properties.

(a) Energy absorption



(b) Axial thermal conductivity



(c) Radial thermal conductivity

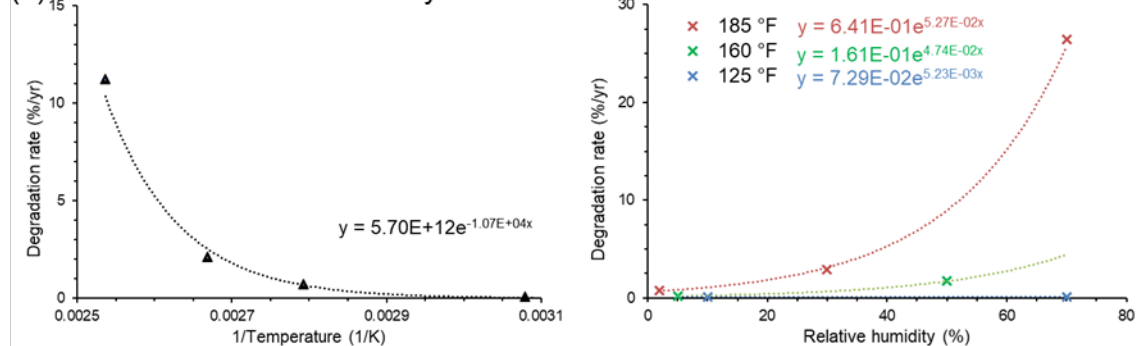


Figure A-12. Plots of degradation rate vs. reciprocal temperature (left) and vs. relative humidity (right) for the identified properties.

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