SUPPLEMENTARY INFORMATION

Physical Aging and Evolution of Mechanical Properties of Additively Manufactured Polyethylene Terephthalate Glycol

Sierra F. Yost,[a] Jordan C. Smith,[b] Christian W. Pester,[c] Bryan D. Vogt[a,*]

[a]Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802
[b]Department of Mechanical Engineering, The Pennsylvania State University, University Park, PA 16802
[c]Department of Materials Science & Engineering, University of Delaware, Newark, DE, 19716

*To whom correspondence should be addressed: bdv5051@psu.edu (B.D.V.)

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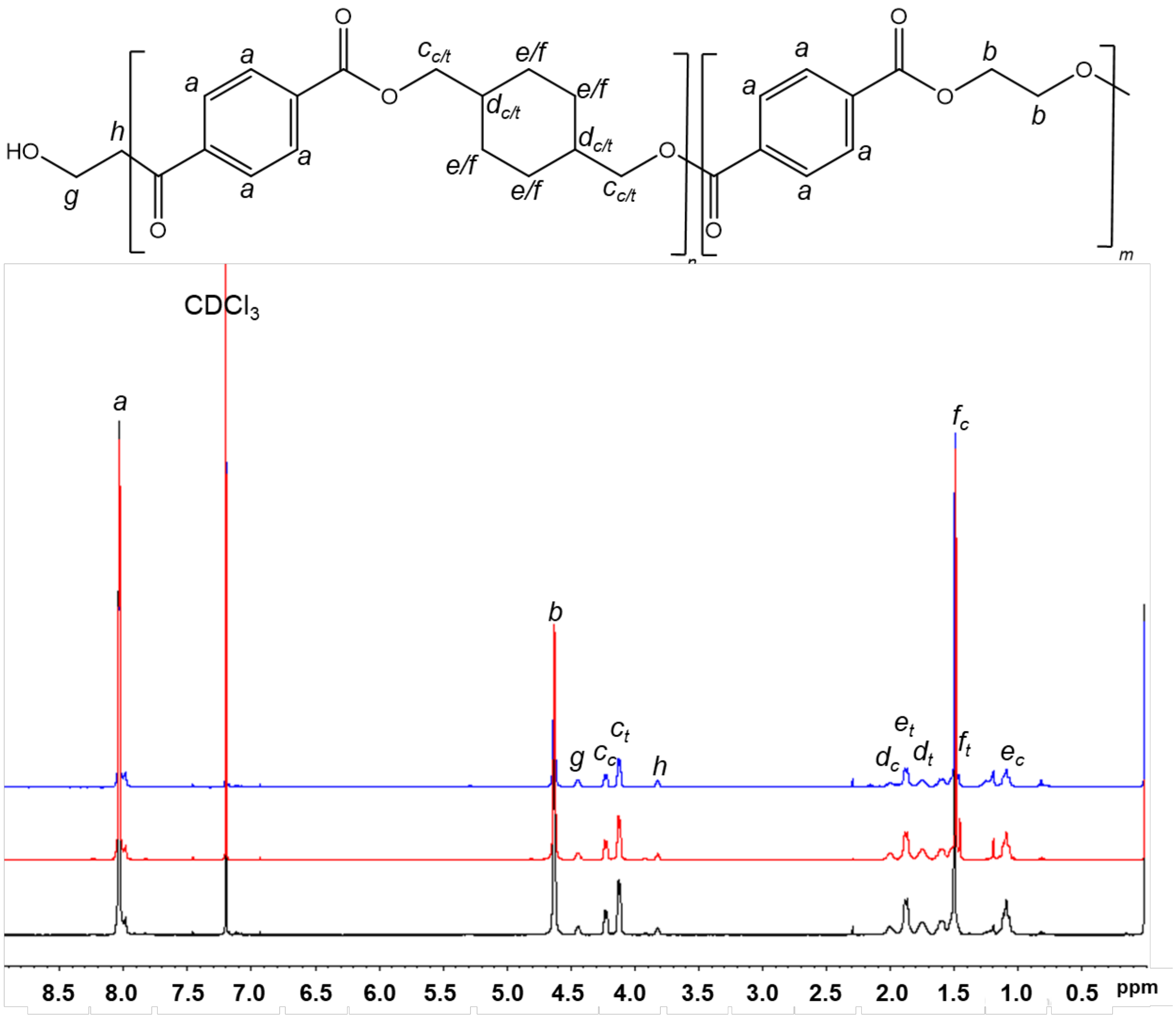

Figure S1. NMR traces for Polymaker (blue), Hatchbox (red), and Overture (black) samples with chemical shifts labeled by proton including differences for cis (*c*) and trans (*t*) conformations.

The relative composition of the copolymers was calculated based on a reference integral peak of 1 at 7.99, denoted by *a*, which represents the 4 protons in the benzene ring. The relative integral of the peaks at 4.6 ppm, denoted by b, represents the 4 protons associated with ethylene glycol. The sum of the relative integrals at 1.85, 1.5, 1,48, and 1.09 (e_t, f_c, f_t, *and* e_c) were represent the 8 protons in the cyclohexane found in the CHDM group. The ratios of the integrals divided by the number of protons they represented were used to determine relative composition. The cis/trans ratios for the Polymaker, Hatchbox, and Overture filaments were 33/67, 32/68, and 33/67 respectively, calculated by the ratio of the integrals for the peaks at e_t and e_c (1.85 and 1.09 ppm, respectively). The molecular mass (M_n) of the copolymers was determined via end group analysis. Degree of polymerization was determined by the ratio between the sums of the relative integrals at 4.43 and 3.82, denoted by *g* and *h*, respectively, which represents the 8 protons associated with the end groups, and the relative integral of the 4 protons on the benzene ring (peak *a*). From the molar masses of the two repeat units (terephthalic acid with ethylene glycol and terephthalic acid with CHDM) and the relative ratios of the two determined above, the average molar mass for each copolymer was determined. M_n was calculated by multiplying the average molar mass by the degree of polymerization for each copolymer.

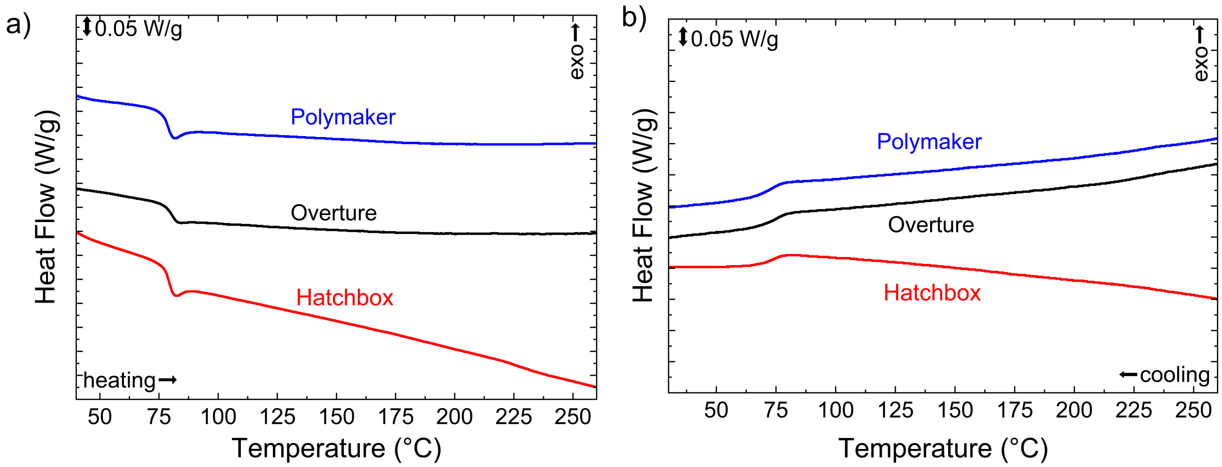

Figure S2. DSC thermographs for Overture, Polymaker, and Hatchbox samples demonstrating no evidence for crystallization when (a) heated at 10 ℃ min^{-1} and (b) cooled at 5 ℃ min^{-1}.

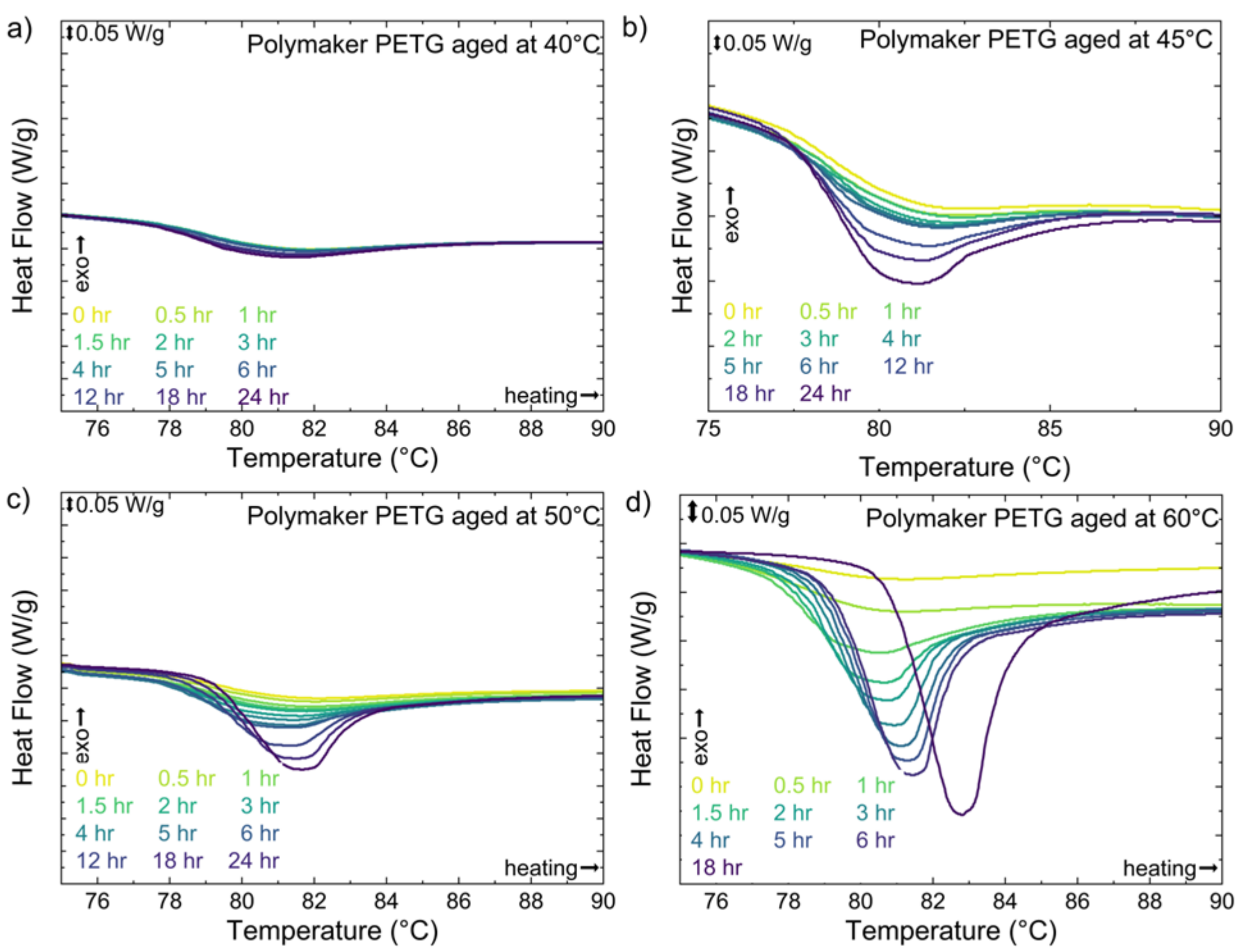

Figure S3. DSC thermographs for Polymaker PETG after aging at (a) 40°C, (b) 50°C, and (c) 60°C at a heating rate of 10℃ min^{-1}.

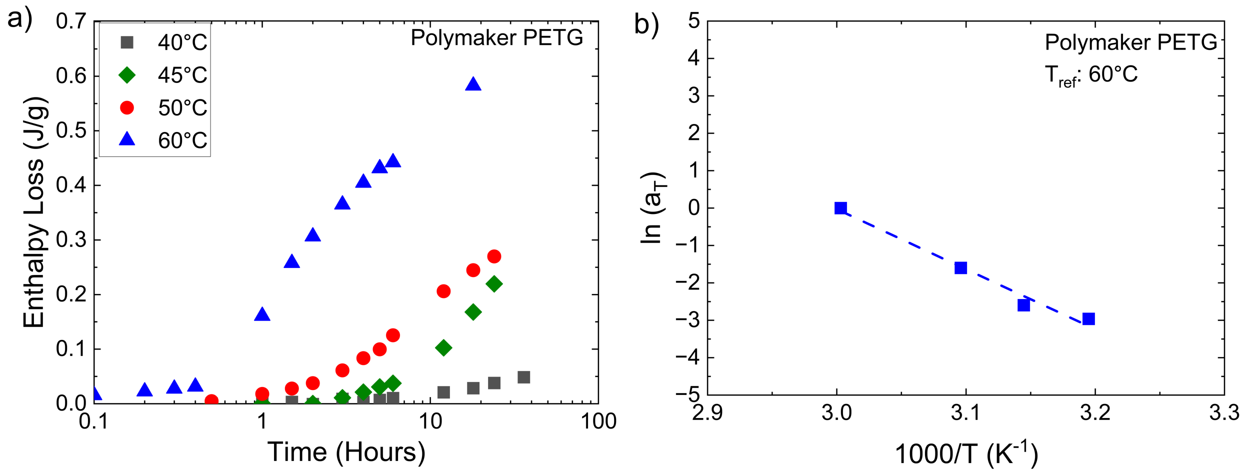

Figure S4. (a) Enthalpy loss for Polymaker PETG. (b) Arrhenius fit of the shift factors for Polymaker PETG at reference temperature of 60°C.

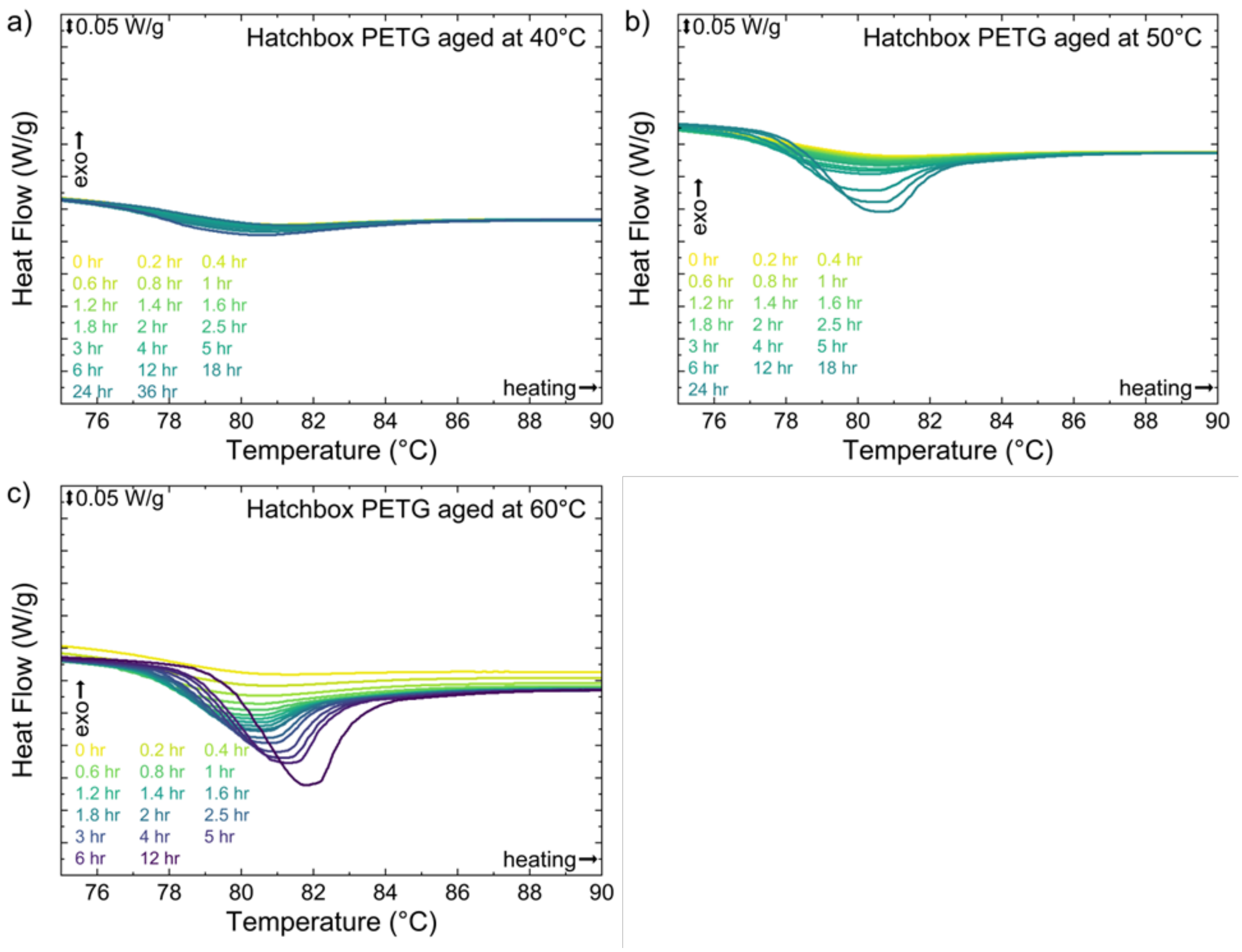

Figure S5. DSC thermographs for Hatchbox PETG after aging at (a) 40 °C, (b) 50 °C, and (c) 60 °C at a heating rate of 10 °C min^{-1}.

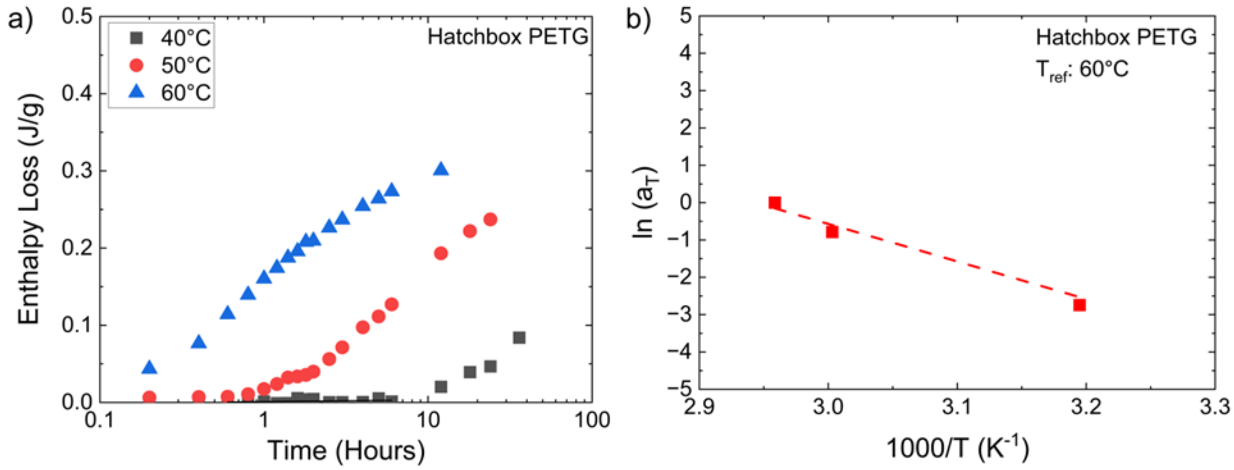

Figure S6. (a) Enthalpy loss for Hatchbox PETG. (b) Arrhenius fit of the shift factors for Hatchbox PETG at a reference temperature of 60°C.

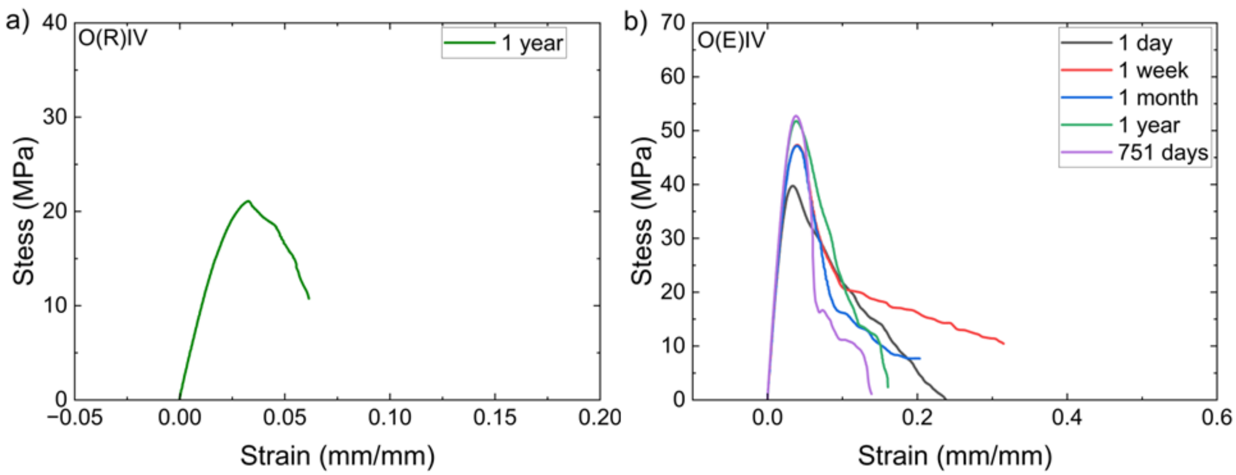

Figure S7. Representative stress- strain curves for (a) O(R)IV and (b)O(E)IV at different aging times.

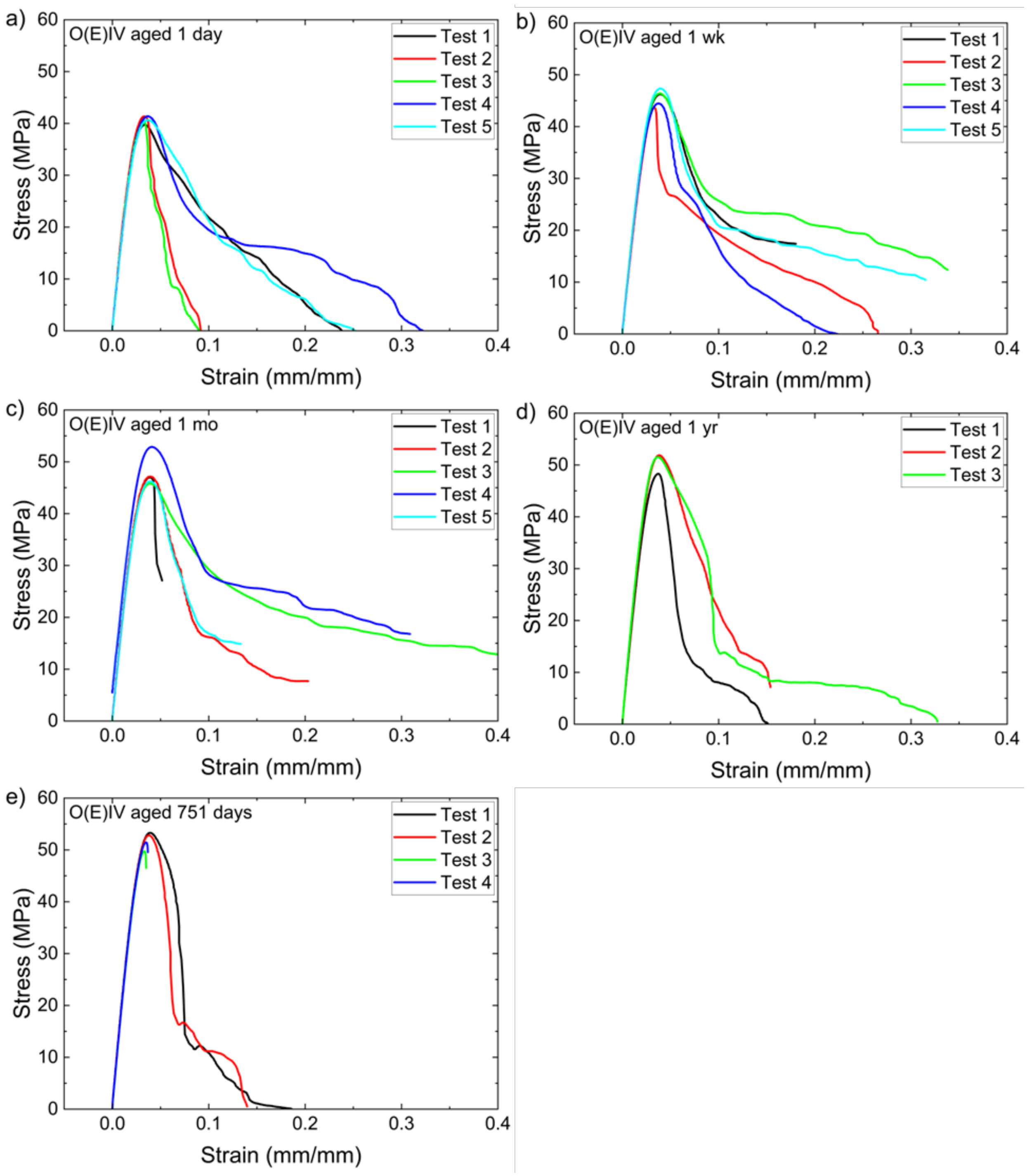

Figure S8. Stress-strain curves for Type IV Overture PETG, O(E)IV, after aging at 60 °C for equivalent of (a) 1 day, (b) 1 week, (c) 1 month, (d) 1 year, and (e) 751 days at 25 °C. The different colors on each curve represent a duplicate sample with the same printing conditions and aging time.

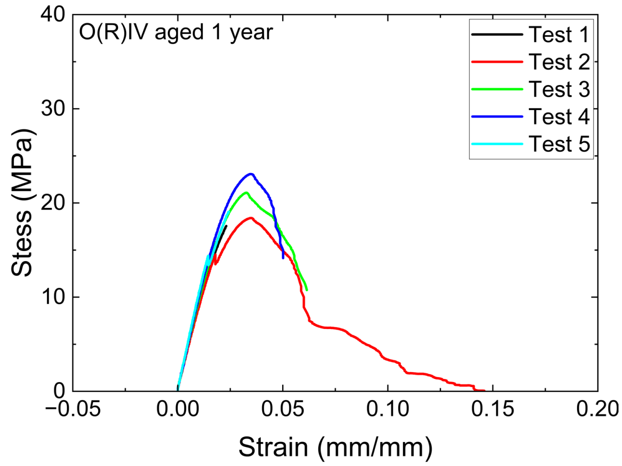

Figure S9. Stress-strain curves for Overture Type IV tensile bars, (O(R)IV), after aging at 60 °C for the equivalent of 1 year at 25 °C.

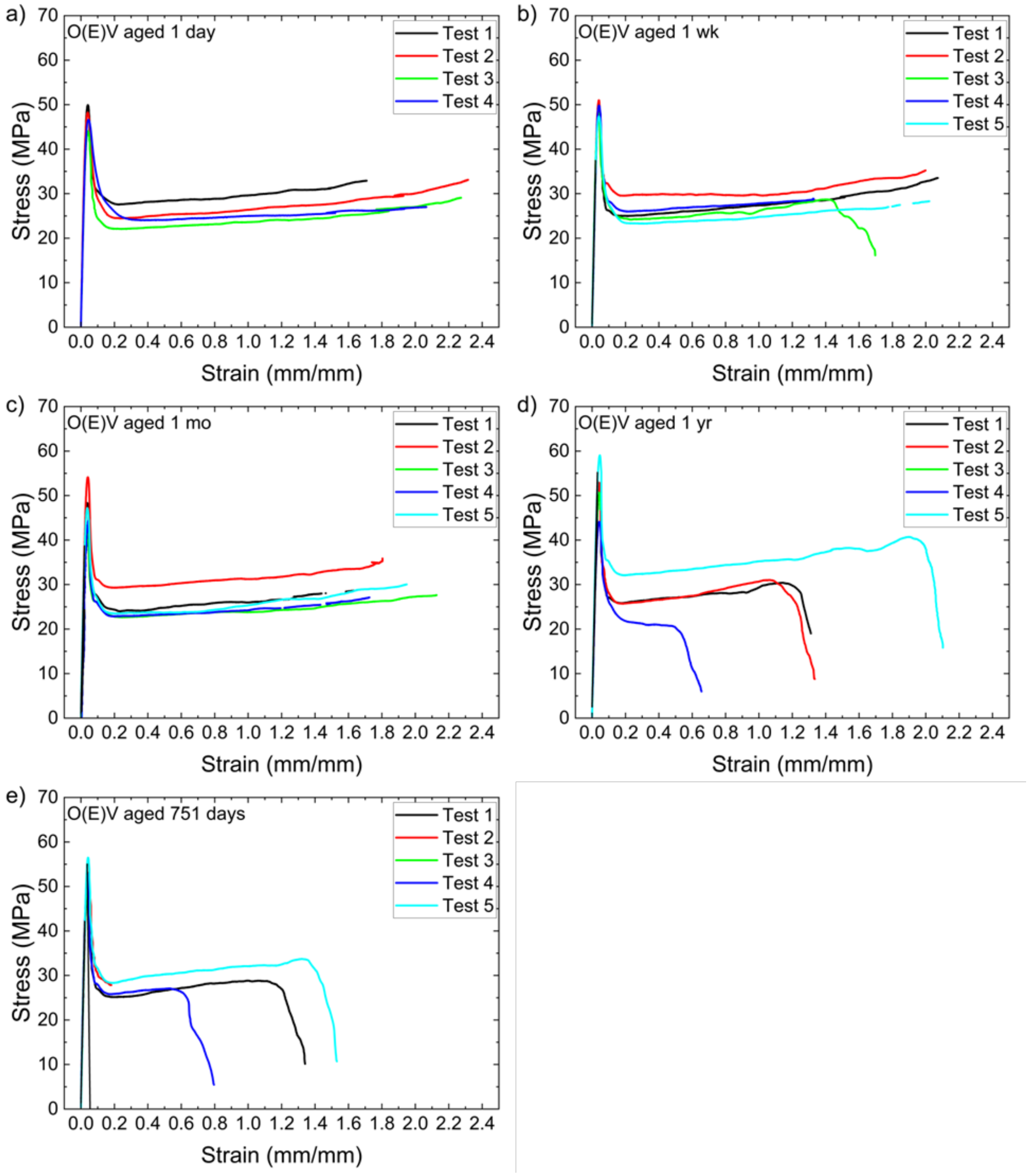

Figure S. Stress-strain curves for Type V Overture PETG, (O(E)V), after aging at 60 °C for an equivalent of (a) 1 day, (b) 1 week, (c) 1 month (d) 1 year, and (e) 751 days at 25 °C.

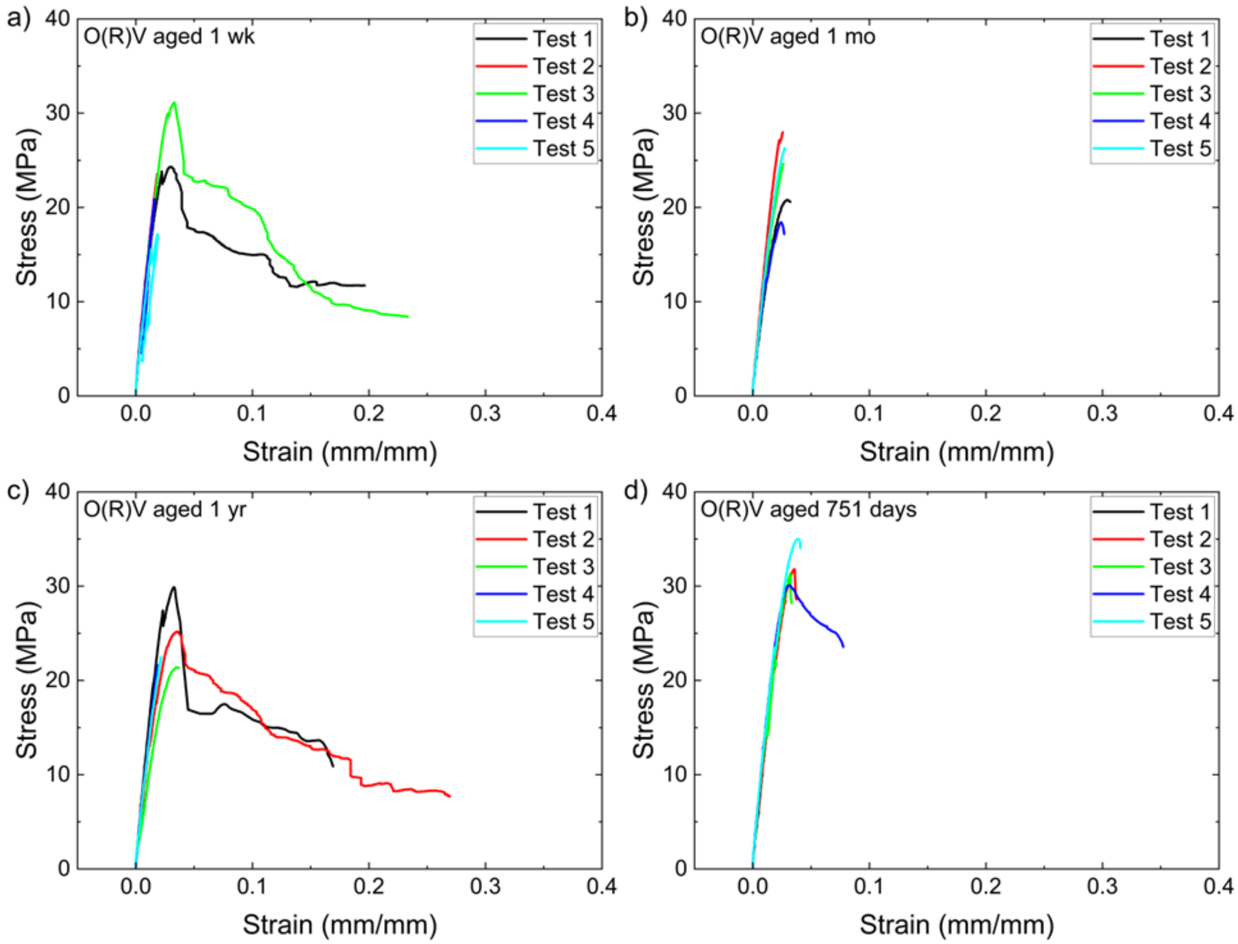

Figure S10. Stress-strain curves for Overture Type V tensile bars, (O(R)V), after aging at 60 °C for the equivalent of (a) 1 week, (b) 1 month, (c) 1 year, and (d) 751 days at 25 °C.

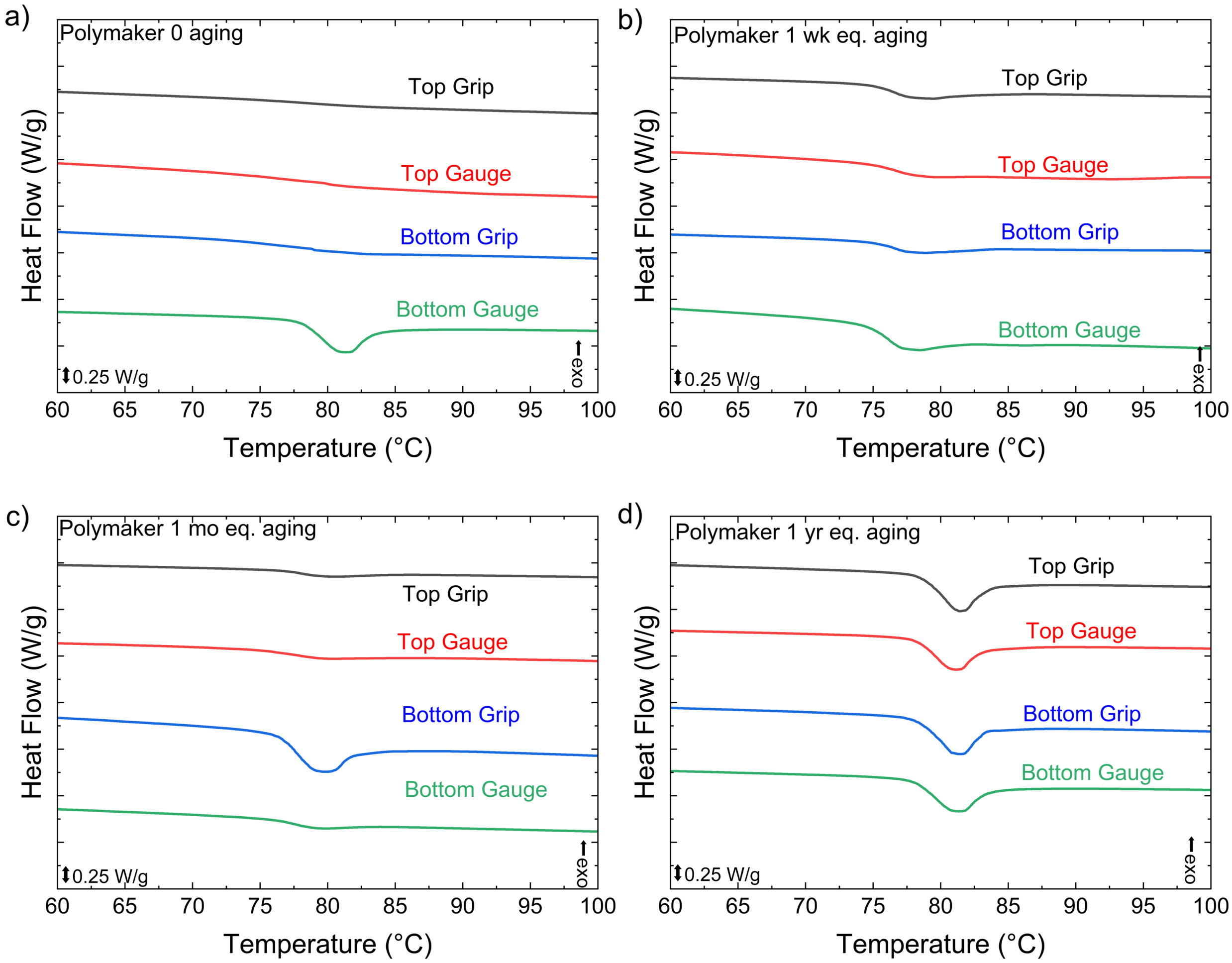

Figure S11. DSC thermographs for Polymaker PETG samples taken from different sections of the printed tensile bar and aged for a) no time, b) the equivalent of 1 week, c) the equivalent of 1 month, and d) the equivalent of 1 year at 25 °C. The accelerated aging of the printed samples was performed at 60°C

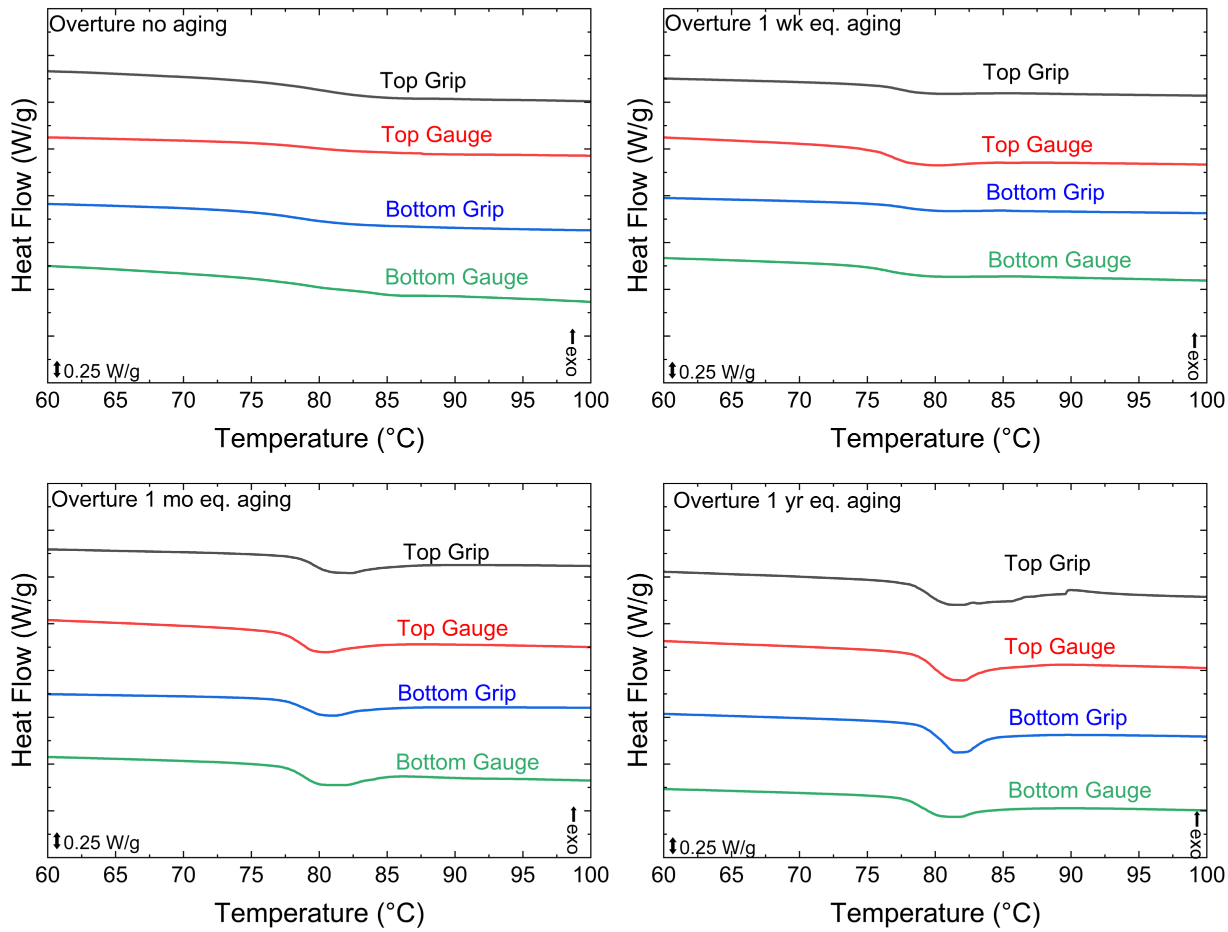

Figure S12. DSC thermographs for Overture PETG samples taken from different sections of the printed tensile bar and aged for a) no time, b) the equivalent of 1 week, c) the equivalent of 1 month, and d) the equivalent of 1 year at 25 °C. The accelerated aging of the printed samples was performed at 60°C.

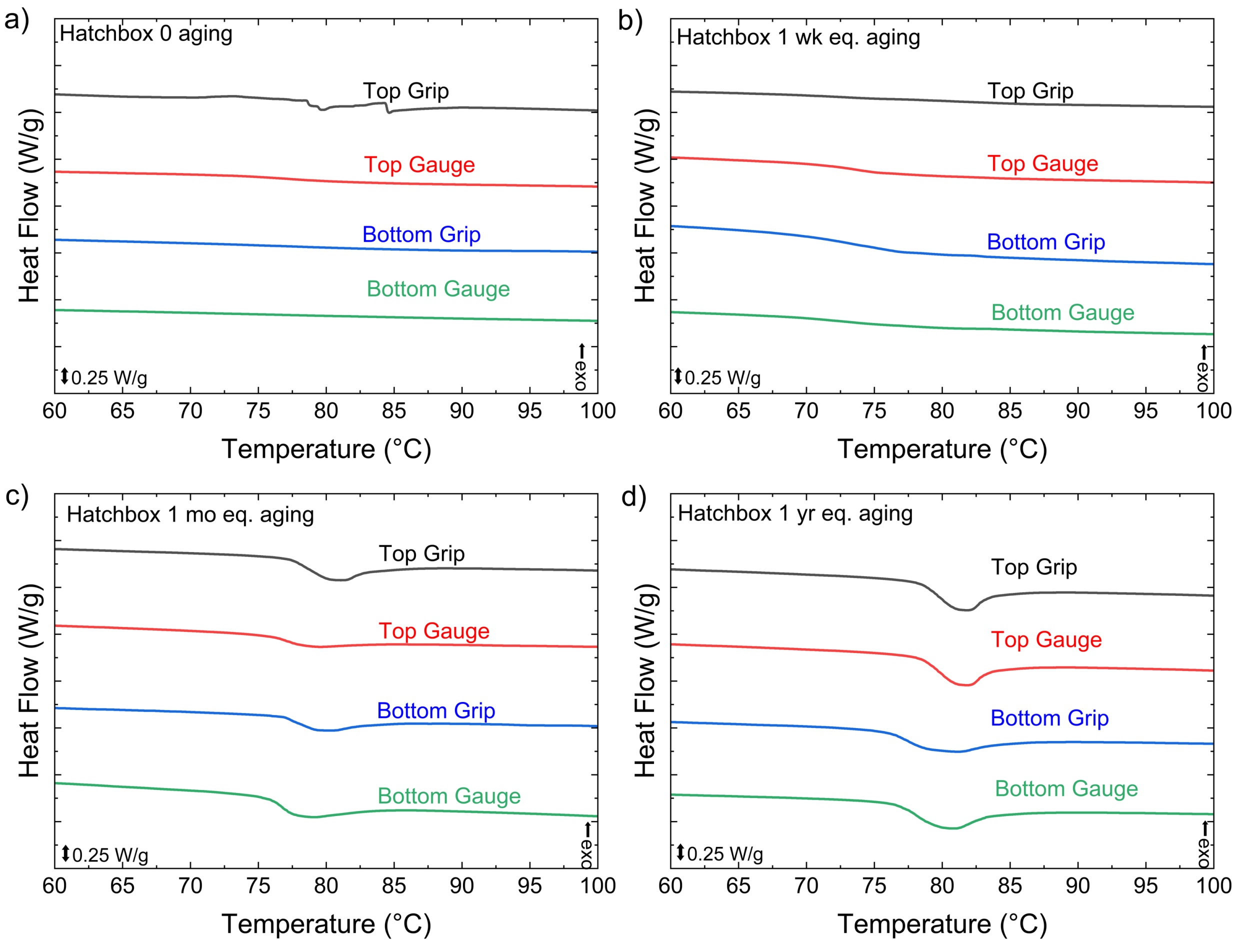

Figure S13. DSC thermographs for Hatchbox PETG samples taken from different sections of the printed tensile bar and aged for a) no time, b) the equivalent of 1 week, c) the equivalent of 1 month, and d) the equivalent of 1 year at 25 °C. The accelerated aging of the printed samples was performed at 60°C.

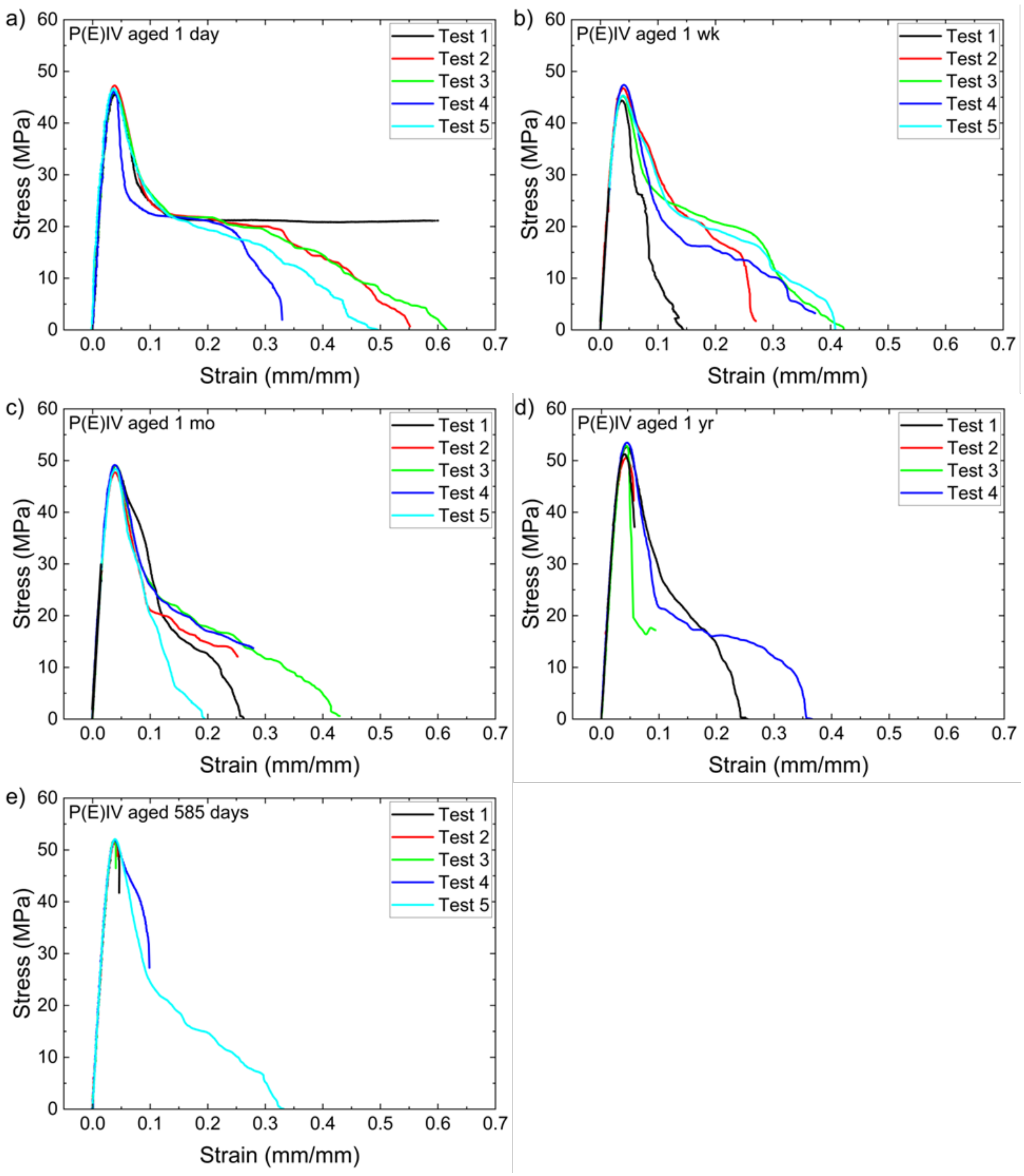

Figure S14. Stress-strain curves for Type IV Polymaker PETG, (P(E)IV), after aging at 60 °C for the equivalent of (a) 1 day, (b) 1 week, (c) 1 month (d) 1 year, and (e) 585 days at 25 °C.

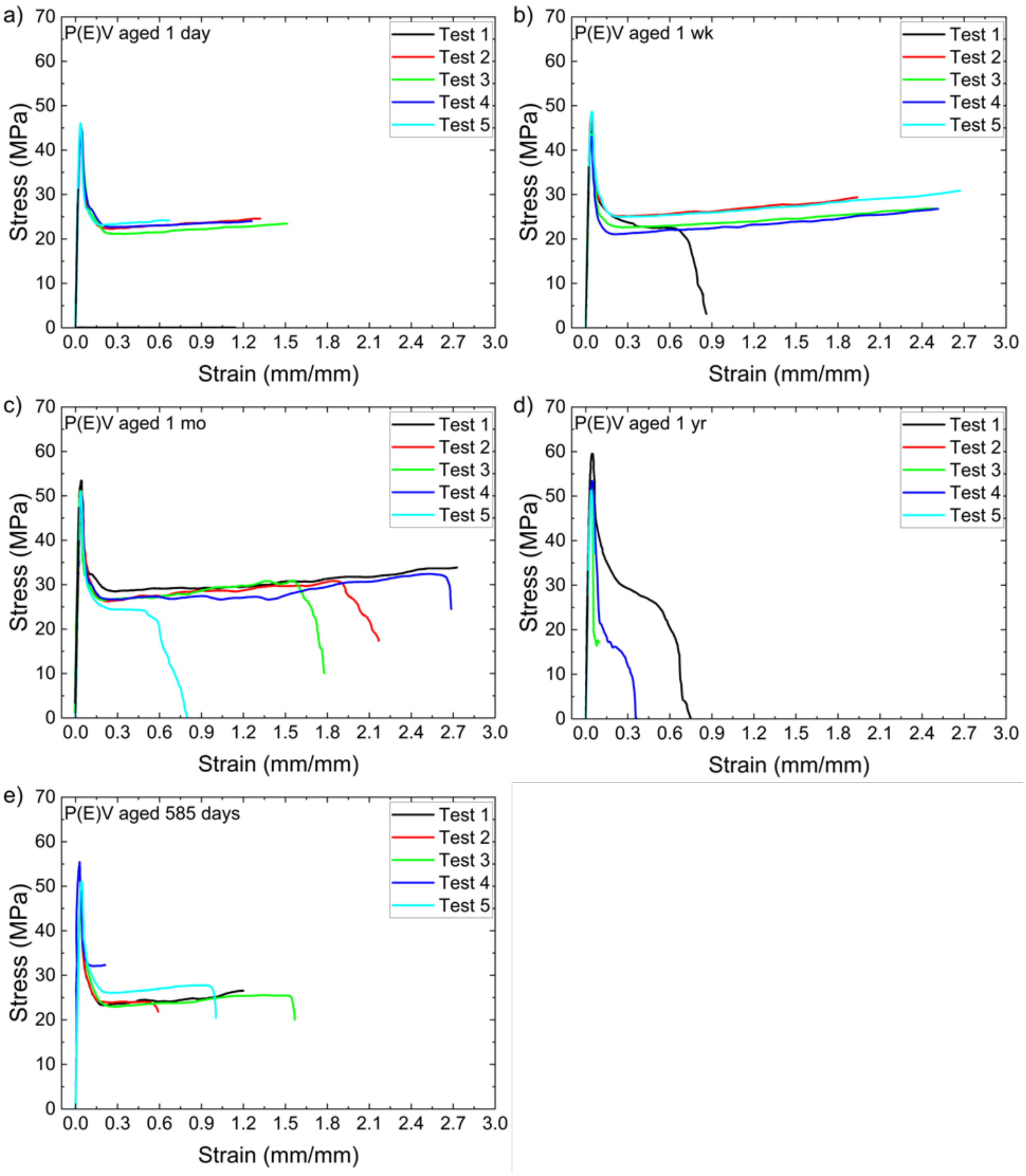

Figure S15. Stress-strain curves for Type V Polymaker PETG, (P(E)V), after aging at 60 °C for the equivalent of (a) 1 day, (b) 1 week, (c) 1 month (d) 1 year, and (e) 585 days at 25 °C.

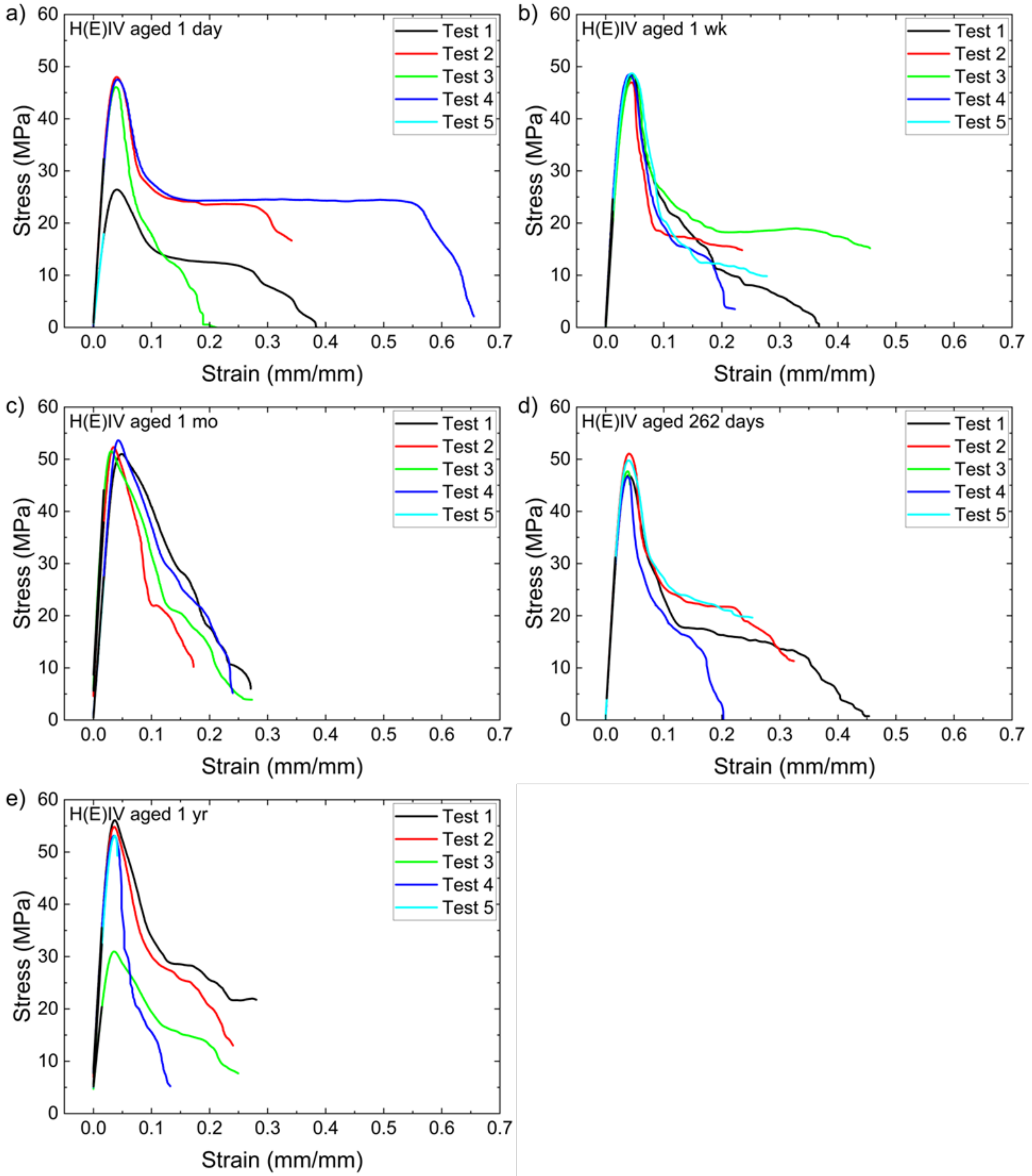

Figure S16. Stress-strain curves for Type IV Hatchbox PETG (H(E)IV) after aging at 60 °C for the equivalent of (a) 1 day, (b) 1 week, (c) 1 month (d) 252 days, and (e) 1 year at 25 °C.

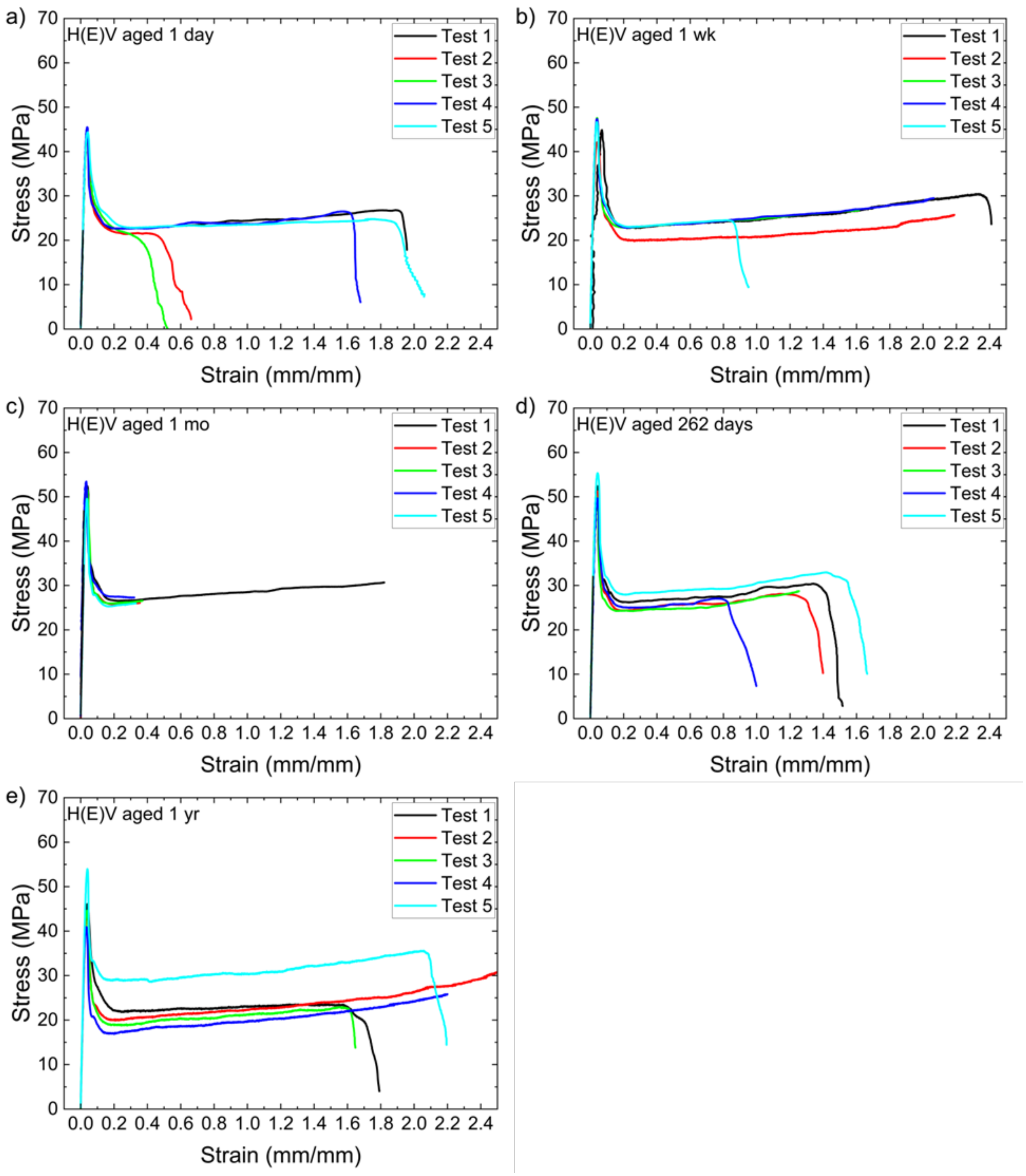

Figure S17. Stress-strain curves for Type V Hatchbox PETG (H(E)V) after accelerated aging at 60 °C for the equivalent of (a) 1 day, (b) 1 week, (c) 1 month (d) 252 days, and (e) 1 year at 25 °C.

Influence of Humidity on Mechanical Properties

Humidity is another factor that can significantly influence polymer aging, but this is not just physical aging, but polymer degradation via hydrolysis. Moisture in the environment can accelerate degradation of the PETG beyond typical physical aging by cleaving ester bonds.[56] This reduces the molecular weight and increases brittleness. PETG is more hygroscopic than PET, meaning it can absorb greater amounts of water due to the increased flexibility of its polymer chains.[55] However, at the aging time scale examined in this paper, humidity did not play a role in aging. Overture PETG Type V printed specimens were used to confirm this due to the intermediate concentration of CHDM. They were aged under accelerated conditions equivalent to one month and one year in a humidity chamber maintained at 80% relative humidity. Figure S12 has the stress strain curves for the tensile bars pulled after being aged in these conditions. As shown in Figure S11, there is no significant difference in the mechanical properties of the Overture PETG samples that were aged in a vacuum or aged at 80% humidity for the same amount of time.

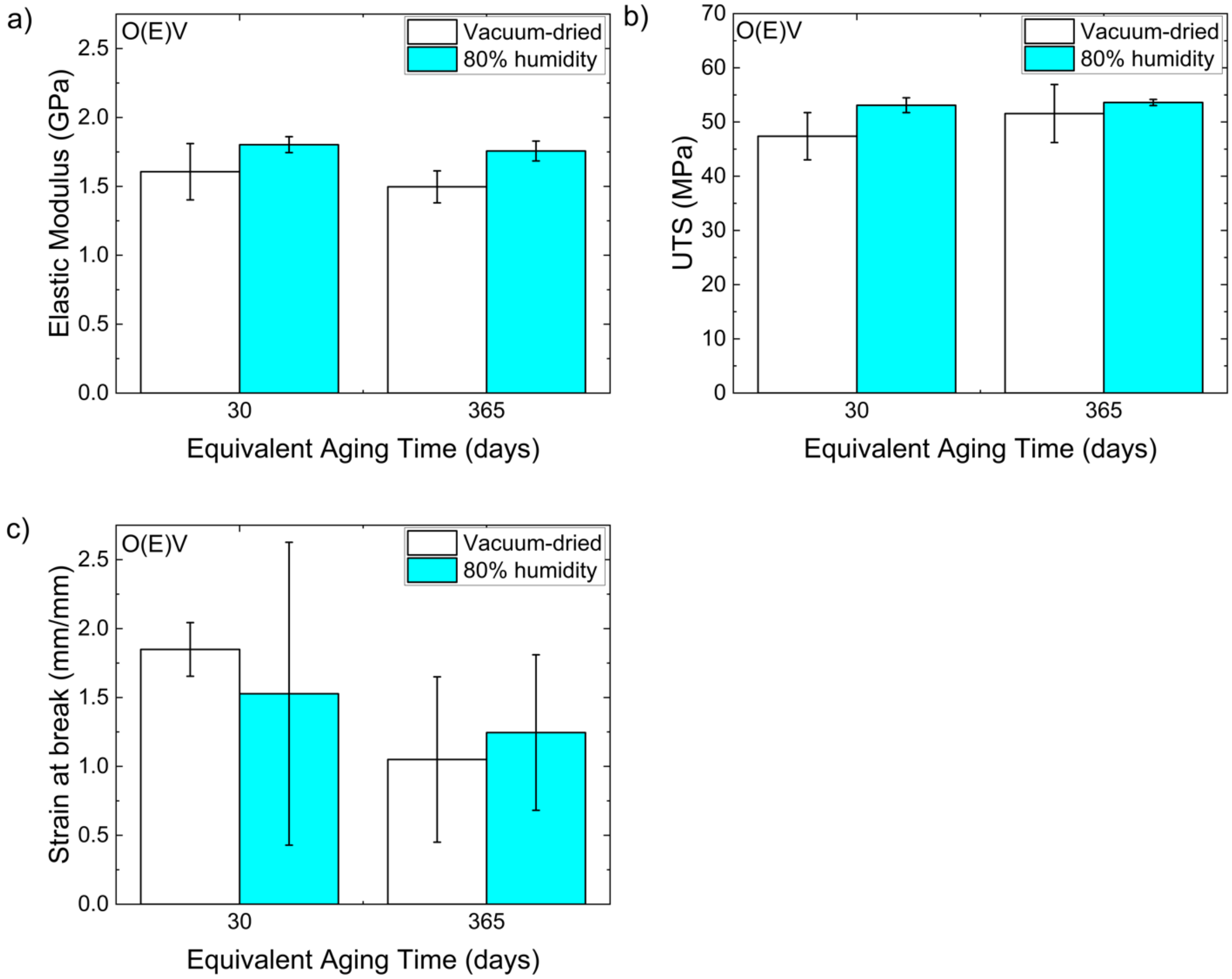

Figure S18:Role of humidity on a) elastic modulus, b) ultimate tensile strength, and c) strain at break for Overture Type V tensile bar aged for the filament equivalent of 1 month and 1 year at 25 °C.

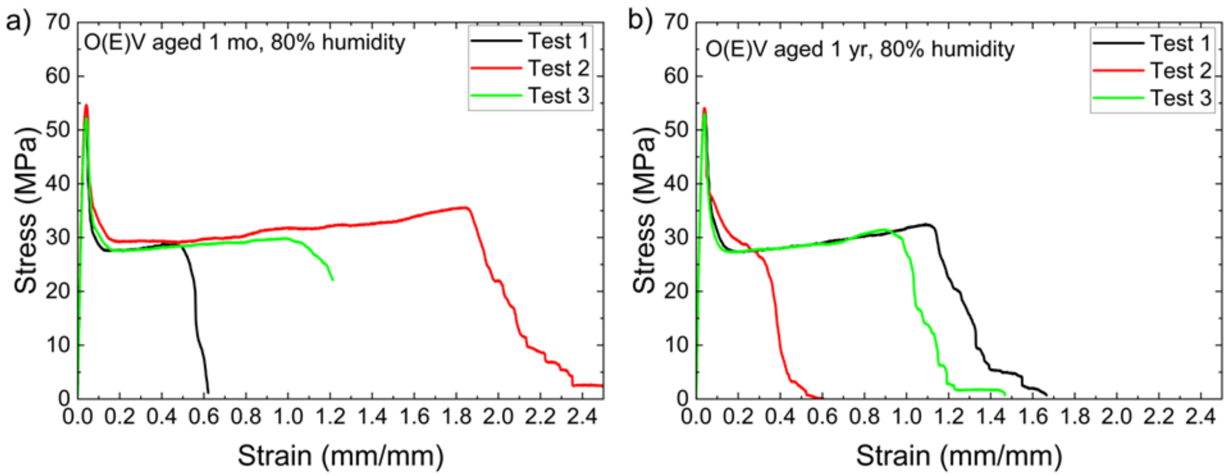

Figure S20. Stress-strain curves for Overture Type V tensile bars aged in 80% relative humidity conditions, after aging for the equivalent of a) 1 month and b) 1 year at 25 °C.