Highly Stable Petroleum Pitch Provides Access to the Deep Glassy State

Heedong Yoon[1], James Heinzman[1], Stuart E. Smith[2], Manesh Gopinadhan[2], Kazem V. Edmond[2], Amy C. Clingenpeel[2], and Nicolas J. Alvarez[1*]

Version of 14 November 2023

Affiliations
1. Department of Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104
2. ExxonMobil Technology and Engineering Company, Annandale, NJ 08801

Analysis

Figure S1 describes the structural relaxation of a typical glass-forming system during isothermal aging. The fictive temperature T_f is defined by the crossover point of the extrapolated equilibrium liquid and the glass lines of enthalpy or volume curves. T_f is generally determined from heat flow curves in calorimetric measurements.[1,56] When the heating and cooling rates are the same, one obtains the limiting fictive temperature T_f' corresponding to T_g. The T_f decreases with increasing aging time, and eventually the T_f approaches the value of the aging temperature T_a.

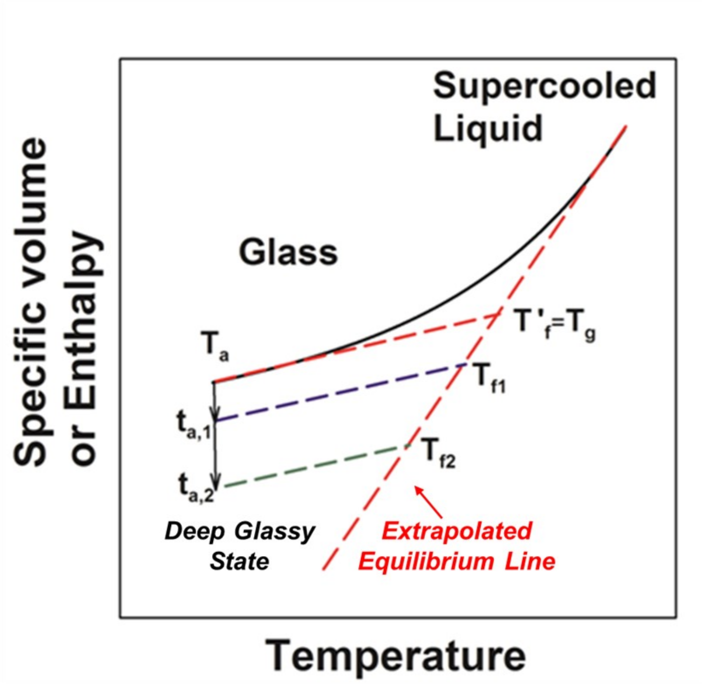

Figure: S1. Schematic diagram of specific volume or enthalpy as a function of temperature for the glass-forming system. The plot shows how the volume or enthalpy evolve towards equilibrium during isothermal aging—reprinted with permission from McKenna and Zhao[7] Copyright 2015 Elsevier.

Intrinsic Isotherms: Down Jump Experiments

One way to look at the structural recovery process of a glassy material is to monitor the enthalpy evolution of the sample by performing down-jump experiments. This experiment is also known as the material's intrinsic isotherm, where the sample is heated above its T_g and then quenched to temperatures below the T_g, and the heat flow response (or enthalpy) is monitored as a function of time. During the isothermal-annealing process, the enthalpy evolves toward an equilibrium state, where the evolution rate depends on the magnitude of the temperature jump (Fig. S2.). The rate typically increases for annealing temperatures approaching T_g, i.e. the rate increases for smaller temperature jumps, and decreases for larger temperature jumps. The red line in Fig. S2 represents the first heating scan and the blue line represents the second heating scan.

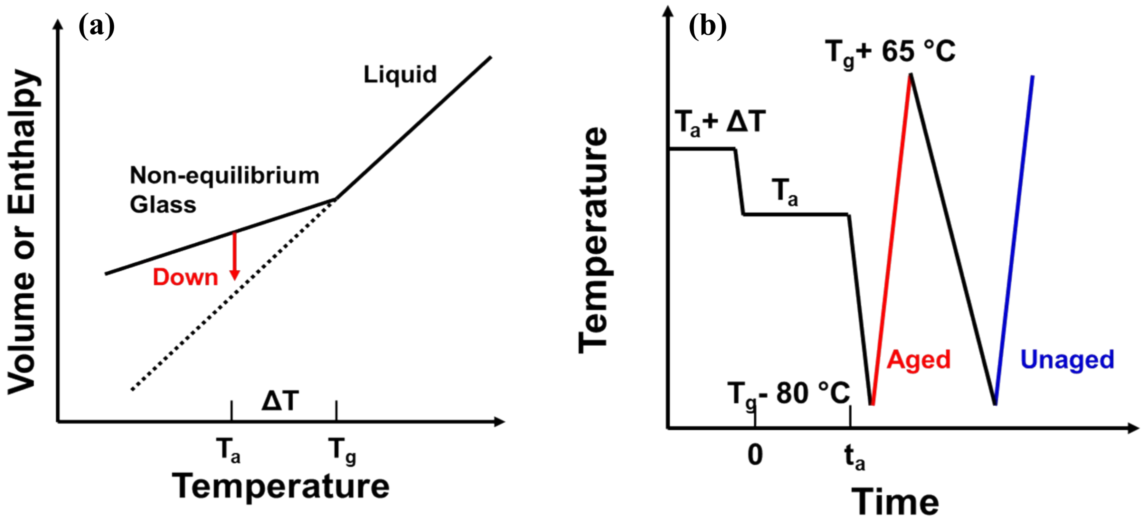

Figure: S2. Schematic diagram[24] of (a) down-jump, and (b) for the DSC measurements.

X-ray Measurements

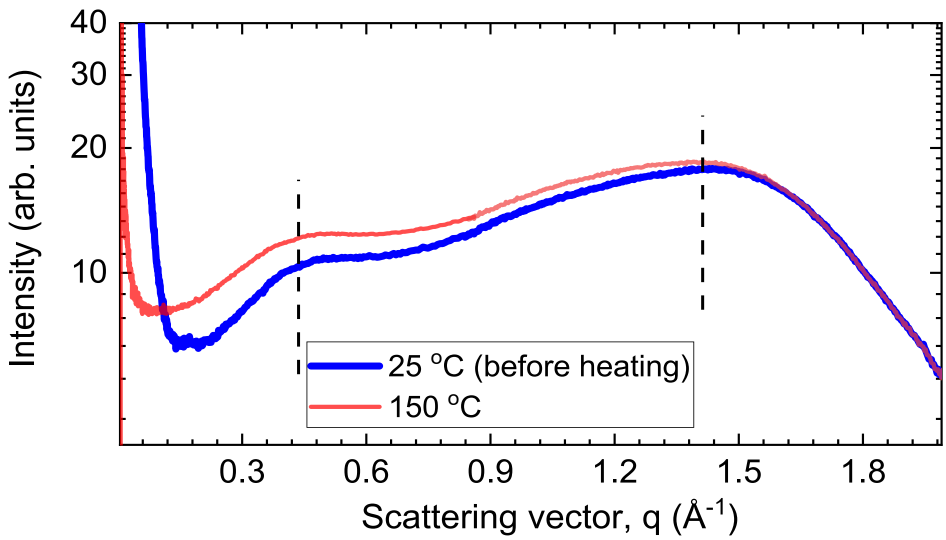

Figure: S3. X-ray data comparison of the unaged sample measured at room temperature (blue line) and measured at 150 °C.

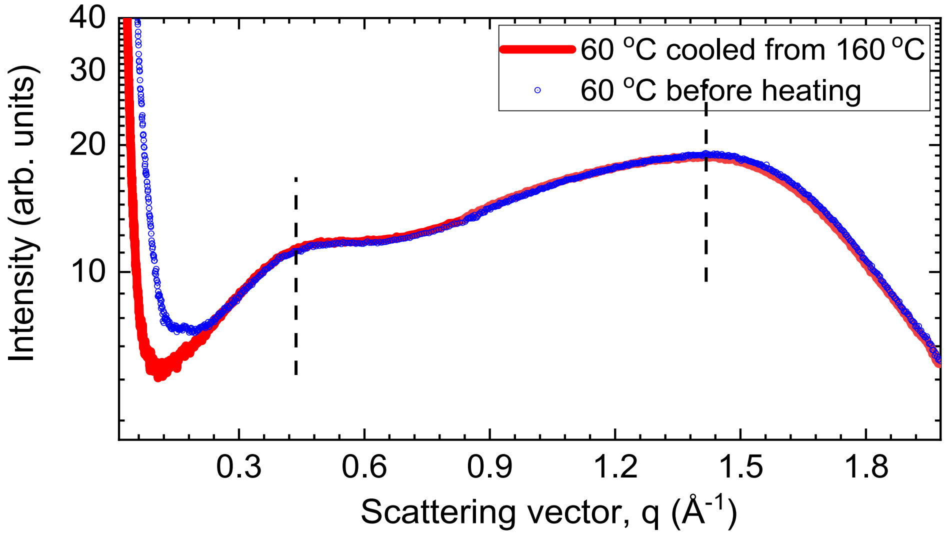

Figure: S4. X-ray data comparison of the aged sample measured at 60 °C (before heating above T_g) and after cooling from 160 °C (10 °C/min). The lower-q and higher-q broad liquid-like peaks did not change in peak position or in intensity after cooling quickly to 60 °C (after erasing the aging history).

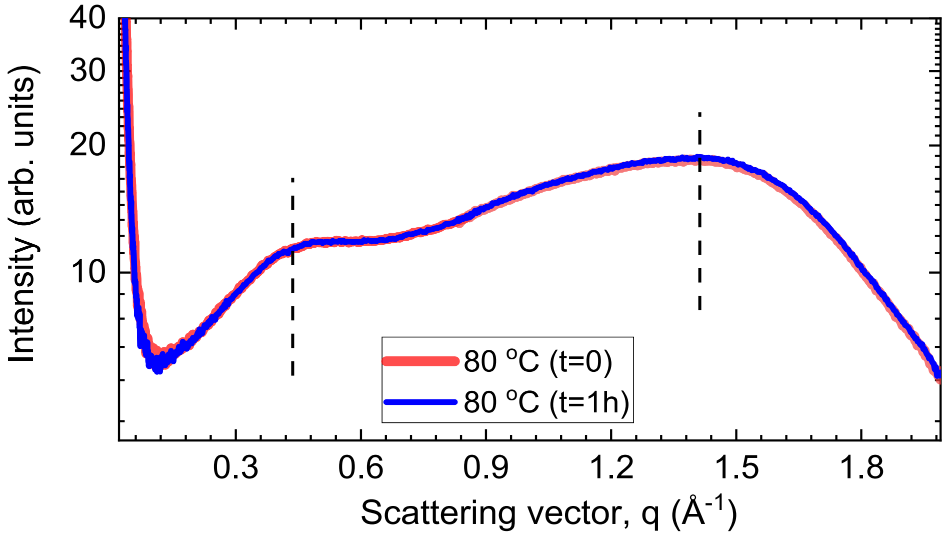

Figure: S5. Isothermal X-ray data of the sample measured at 80 °C after cooling from 160 °C (10 °C/min). There was no change in the X-ray profile after isothermal holding at 80 °C for 1h.

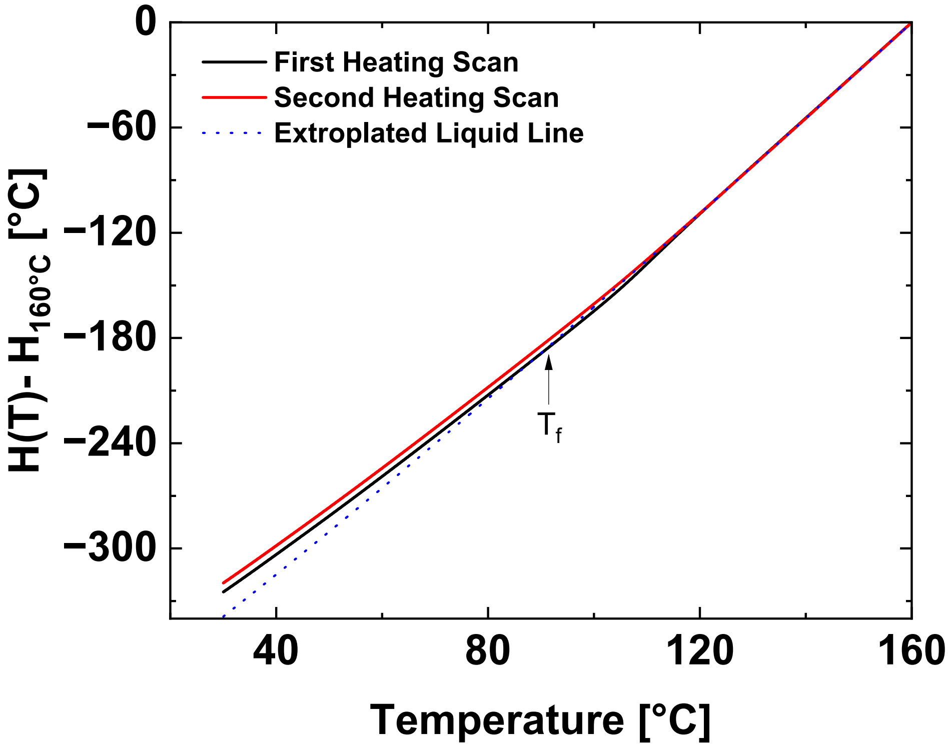

Figure: S6. Enthalpy calculated by integrating the first and second heating curves in Figure 1a.

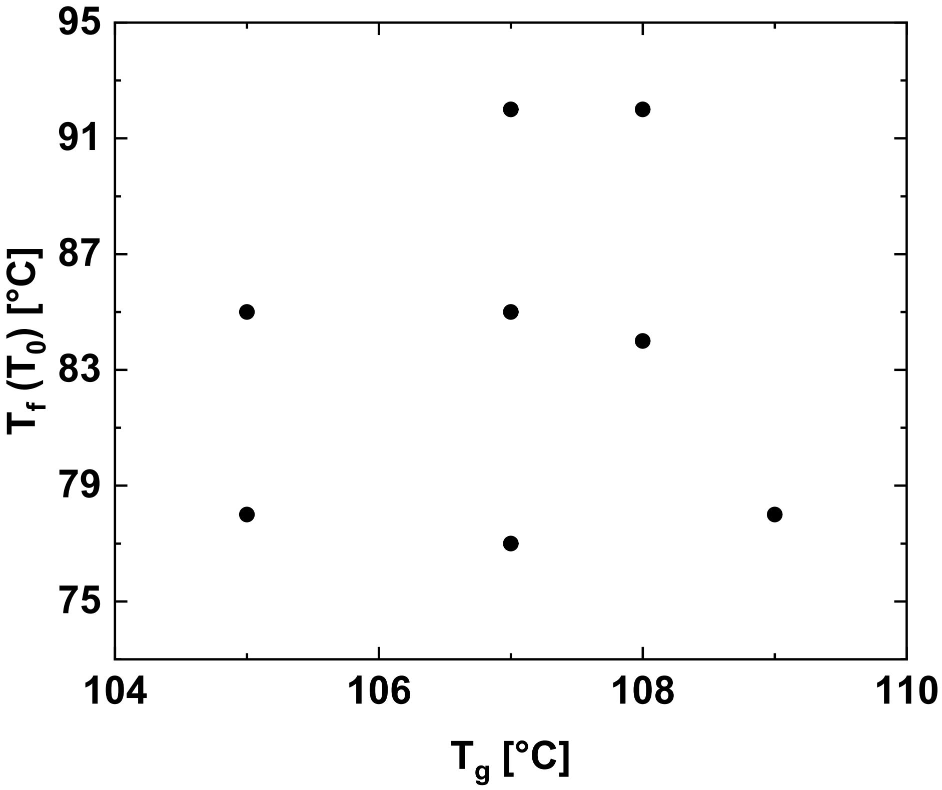

Figure: S7. T_f and T_g measured on nine samples from the same batch. The T_f and T_g were determined from DSC measurements in their first and second heating scans. The T_f and T_g did not show a clear correlation, which shows the sample is heterogeneous.

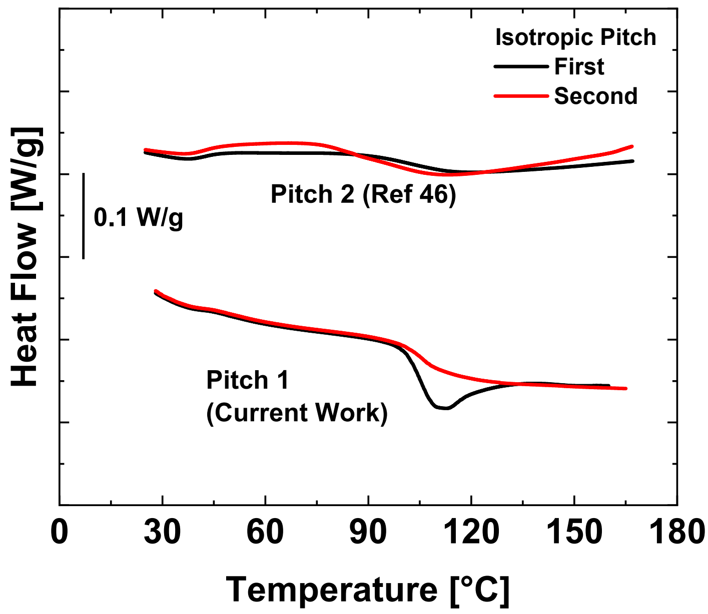

Figure: S8. DSC first and second heating scans of Pitch 1 and Pitch 2, Pitch 2 data is from ref 36 and did not show a large endothermic peak.

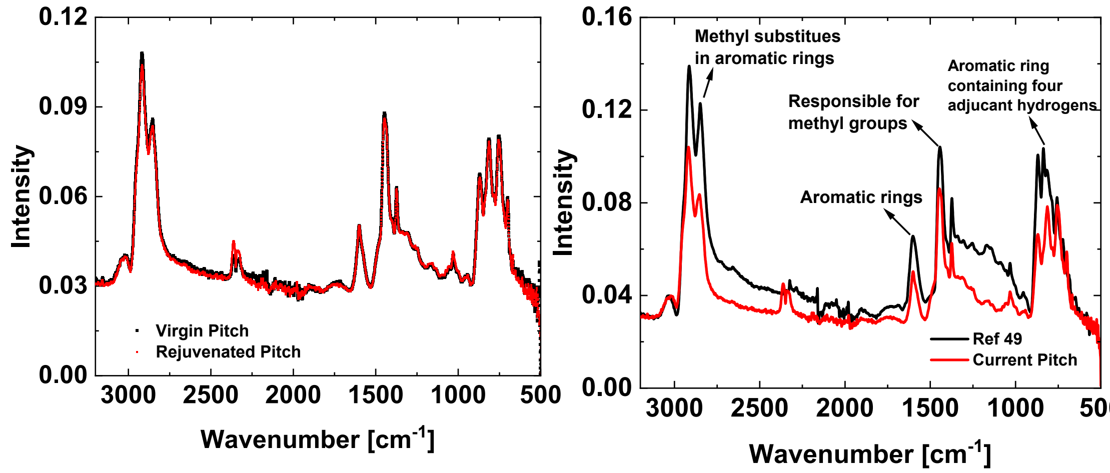

Figure: S9. IR spectra for pitch sample. (a) Comparison aged and rejuvenated Pitch 1, (b) IR spectra of pitch 1 and pitch 2 (reference data Ref 46 is adapted from Yoon et. al. Soft Matter 17, 8925 (2021).

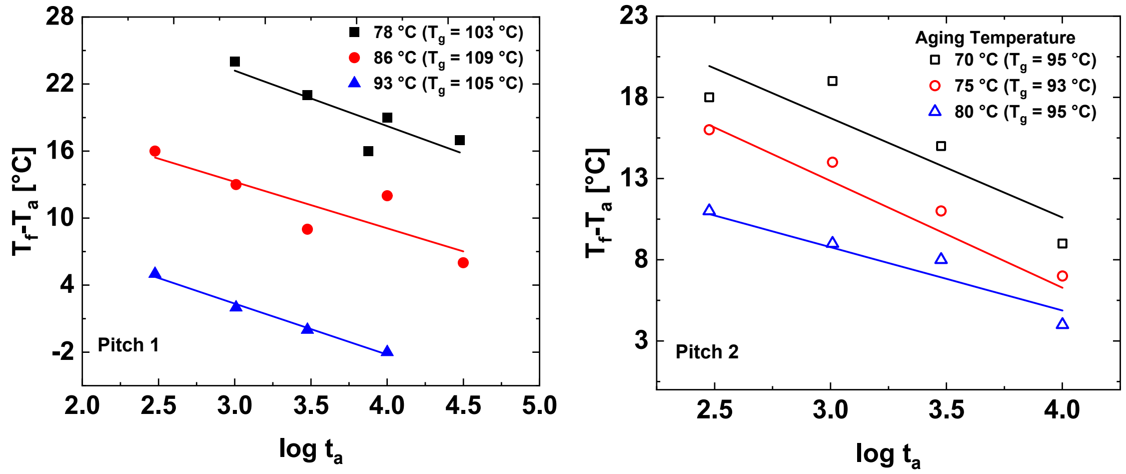

Figure: S10. Departure from equilibrium, T_f-T_a as function of aging time for Pitch 1 (a) and 2 (b) at different temperatures. linear line indicates linear fit of the data to Eq. 3

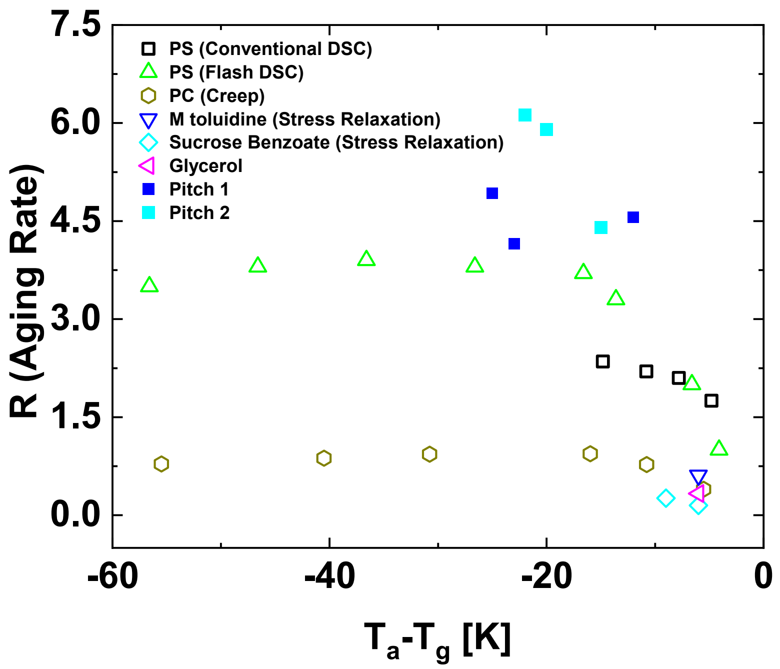

Figure: S11. The aging rate of pitch molecules estimated from Eq. 3 along with the results of polystyrene (PS)[51, 52] polycarbonate (PC)[26], and other small molecular glass-formers[25] reported from the literatures. Note that all experiments at a given annealing temperature were performed on the same sample to avoid inconsistencies due to material heterogeneity.

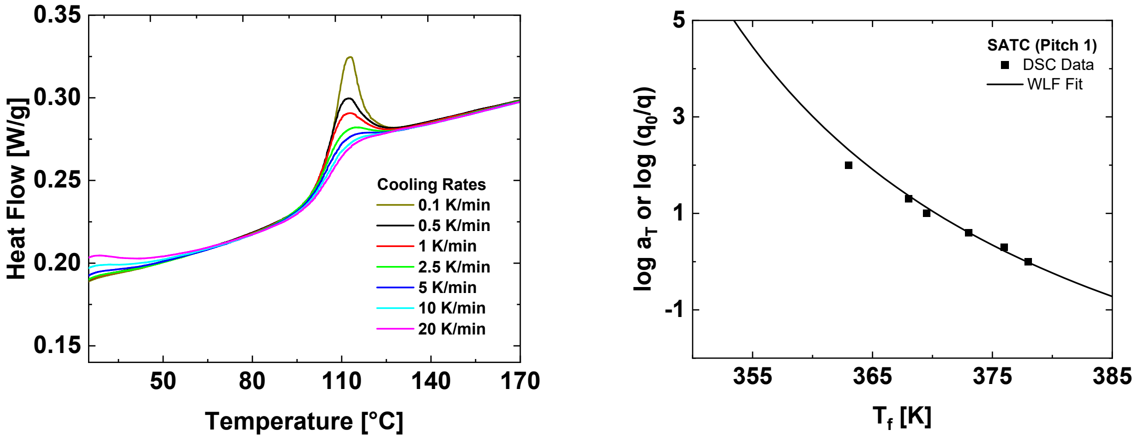

Figure: S12. The cooling rate dependence of T_f for the Pitch. a) Heat flow response of pitch 1 with different cooling rates. b) cooling rate dependence of T_f determined from Moynihan equation from Figure 1a).

Fragility (m)[37-39] describes the temperature dependent relaxation dynamics of glass-forming system (Figure S13). The m is defined by slope of the relaxation (or dynamics) curve at T_g, which can be calculated by following equation:

$$m = \frac{d(\log \gamma)}{d(\frac{T_g}{T})} = \frac{B/T_g}{\ln 10\left(1 - \frac{T_\infty}{T_g}\right)^2} \qquad \text{(S1)}$$

where γ is the relaxation time, B is the fitting parameter, and T_∞ is VFT Temperature. The dynamics (Figure S13) of strong glasses ($m < 50$), are generally less temperature dependent and follows Arrhenius like behavior whereas fragile glasses ($m \geq 100$) are more sensitive to temperature.

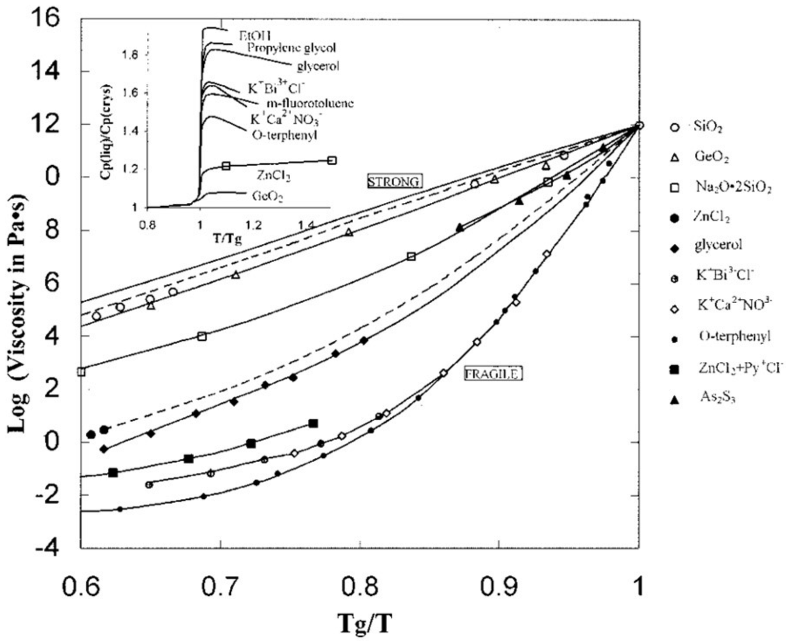

Fig. S13 Fragility (Angell Plot) plot for glass-forming systems. Logarithm of viscosity as function of temperature with strong to fragile liquids. Reprinted and permission from reference 39.

Table S1. Enthalpy difference between virgin and rejuvenated pitch and their corresponding T_f reduction.

Pitch	ΔCp [J/g/K]	ΔH [J/g]	ΔT_f [K]
Sample 1	0.21	8	35
Sample 2	0.22	4	20
Sample 3	0.26	5	18
Sample 4	0.14	4	27
Sample 5	0.14	4	26
Sample 6	0.23	3	14
Sample 7	0.22	4	18
Sample 8	0.21	4	21

Table S2. Enthalpy difference between aged and rejuvenated pitch and their corresponding T_f reduction.

1) T_a = 93 °C, T_g = 105 °C, ΔC_p =0.23 [J/gK]

Pitch 1	5 min	17 min	50 min	167 min	527 min
ΔH [J/g]	1.50	2.77	2.99	3.47	
ΔT_f [K] from ΔH	6.58	12.10	13.07	15.18	
ΔT_f [K] from Moynihan	7	10	12	14	

2) T_a = 86 °C, T_g = 109 °C, ΔC_p =0.22 [J/gK]

Pitch 1	5 min	17 min	50 min	167 min	527 min
ΔH [J/g]	1.50	2.05	3.15	2.17	3.70
ΔT_f [K] from ΔH	6.82	9.32	14.30	9.85	16.81
ΔT_f [K] from Moynihan	7	10	14	11	17

3) T_a = 78 °C, T_g = 103°C (101°C), ΔC_p =0.21 [J/gK]

Pitch 1	17 min	50 min	120 min	167 min	500 min
ΔH [J/g]	0	1	2	1	2
ΔT_f [K] from ΔH	1	4	9	6	10
ΔT_f [K] from Moynihan	1	4	9	6	8

4) T_a = 80 °C, T_g = 95 °C, Δ Cp =0.19 [J/gK]

Pitch 2	5 min	17 min	50 min	167 min
ΔH [J/g]	1	1	1	2
ΔT_f [K] from ΔH	5	6	7	11
ΔT_f [K] from Moynihan	4	6	7	11

5) T_a = 70 °C, T_g = 92 °C, ΔC_p =0.196 [J/gK]

Pitch 2	5 min	17 min	50 min	167 min
ΔH	1	0	1	3
ΔT_f [K] from ΔH	3	2	7	15

ΔT_f [K] from Moynihan	4	3	7	15

6) T_a = 75 °C, T_g = 95 °C, ΔC_p =0.19 [J/gK]

Pitch 2	5 min	17 min	50 min	167 min
ΔH [J/g]	1	1	2	3
ΔT_f [K] from ΔH	4	6	10	14
ΔT_f [K] from Moynihan	4	6	9	13

Table S3. Fragility values of Pitch and other glass-forming materials.

	Pitch 1	Pitch 2[46]	PS[37]	Amber[35]	$Ce_{70}Al_{10}Cu_{20}$[40]	Indomethacin[32]
m	43	53	116	90	28	83