Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Physical Aging of Hydroxypropyl Methylcellulose Acetate Succinate *via* Enthalpy Recovery

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Polymer	T_g (K)
HPMCAS-LF	392.8±0.2K
HPMCAS-MF	393.0±0.2K
HPMCAS-HF	392.7±0.1K
PS (16.4k MW)	373.4±0.2K

Table 1. T_g values of the three grades of HPMCAS, and PS (16.4k MW), used in this study.

$$\int_{T \ll T_g}^{T \gg T_g} (\dot{Q}_{liq} - \dot{Q}_{glass}) dT = \int_{T_f}^{T \gg T_g} (\dot{Q}_{aged} - \dot{Q}_{glass}) dT$$

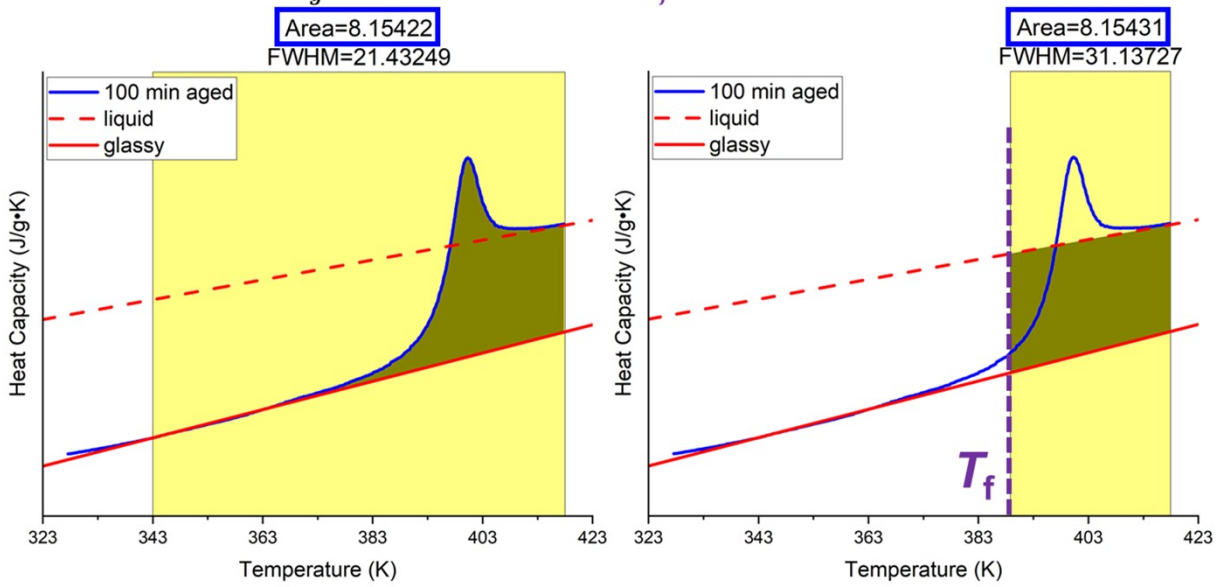

Figure 1. Moynihan method of fictive temperature calculation, where $\dot{Q}_{liq}$ represents the extrapolated liquid heat flow, $\dot{Q}_{glass}$ represents the extrapolated glass heat flow, and $\dot{Q}_{aged}$ represents the heat flow of the aged sample. An example of the Moynihan method using graphical methods is illustrated, where the gray shaded area represents the value of the integrals and the fictive temperature is highlighted in purple.

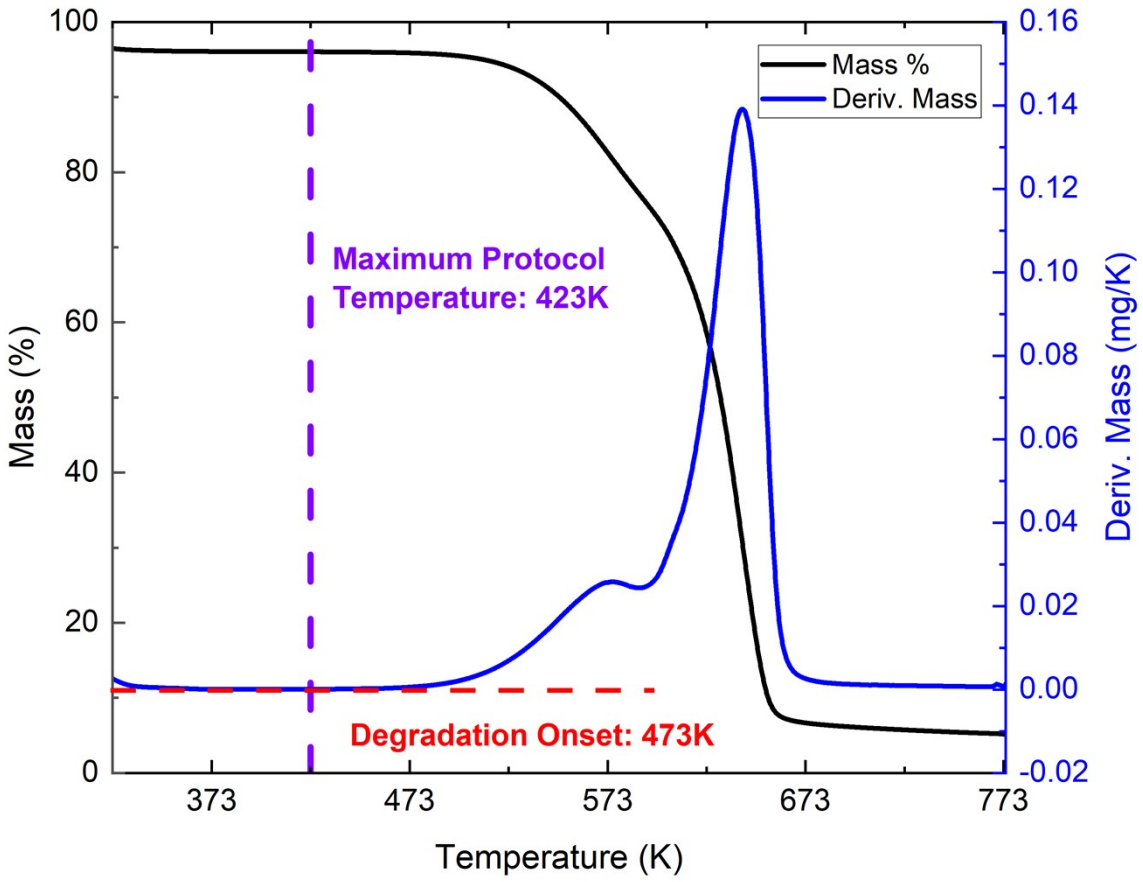

Figure 2. TGA thermogram of HPMCAS-LF. A maximum temperature of 423K was selected to ensure no thermal degradation occurred throughout the aging protocol. The initial approximately 5% mass loss was due to water content removal.

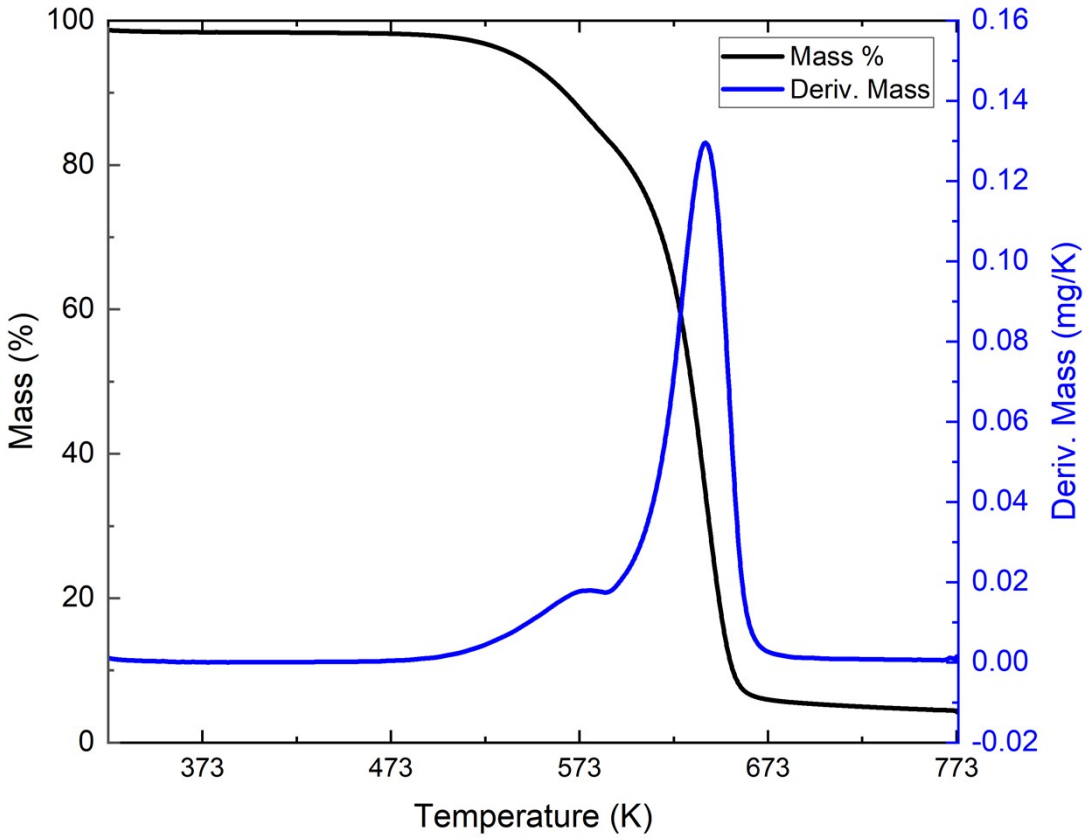

Figure 3. TGA thermogram of HPMCAS-MF, obtained using the same parameters as described in the main text. The initial approximately 3% mass loss was due to water content removal.

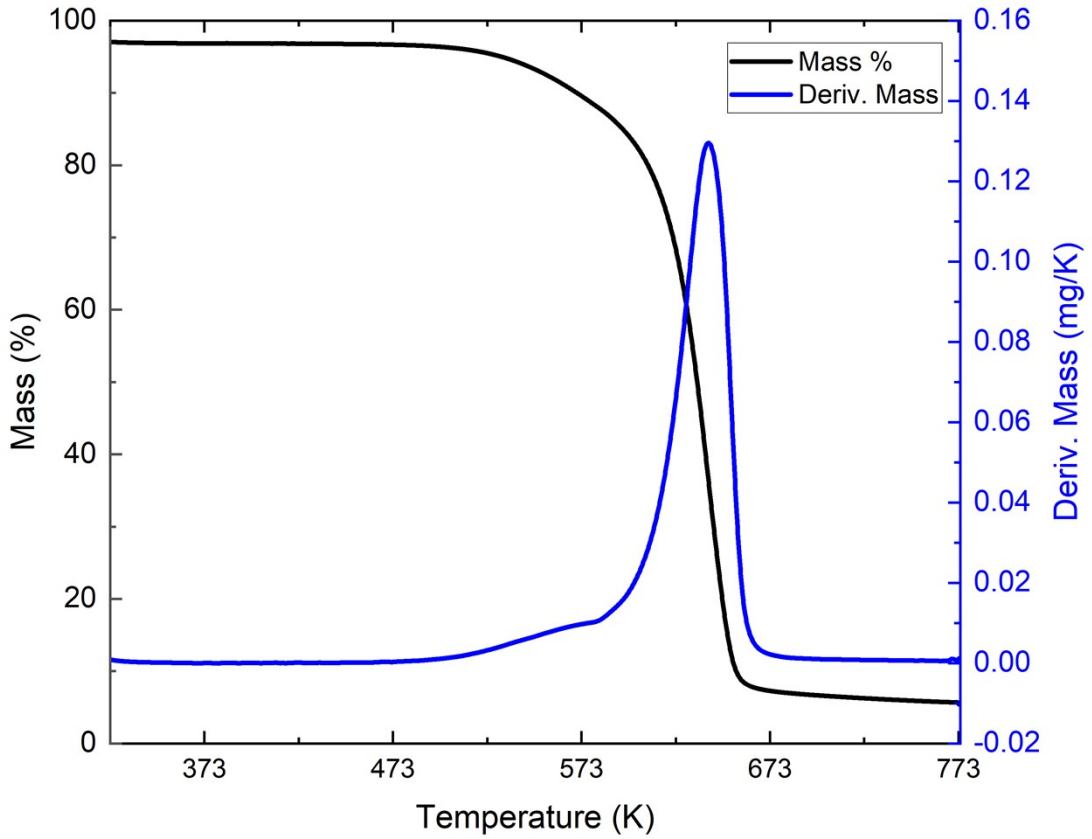

Figure 4. TGA thermogram of HPMCAS-HF obtained using the same parameters as described in the main text. The initial approximately 4% mass loss was due to water content removal.

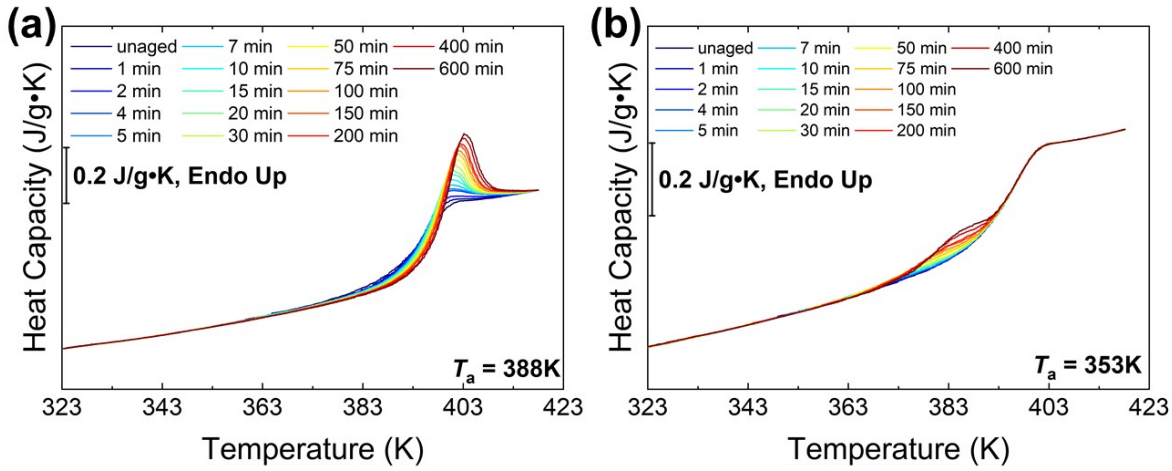

Figure 5. Re-heating thermograms after aging HPMCAS-MF at t_a for T_a = **(a)** 388K and **(b)** 353K.

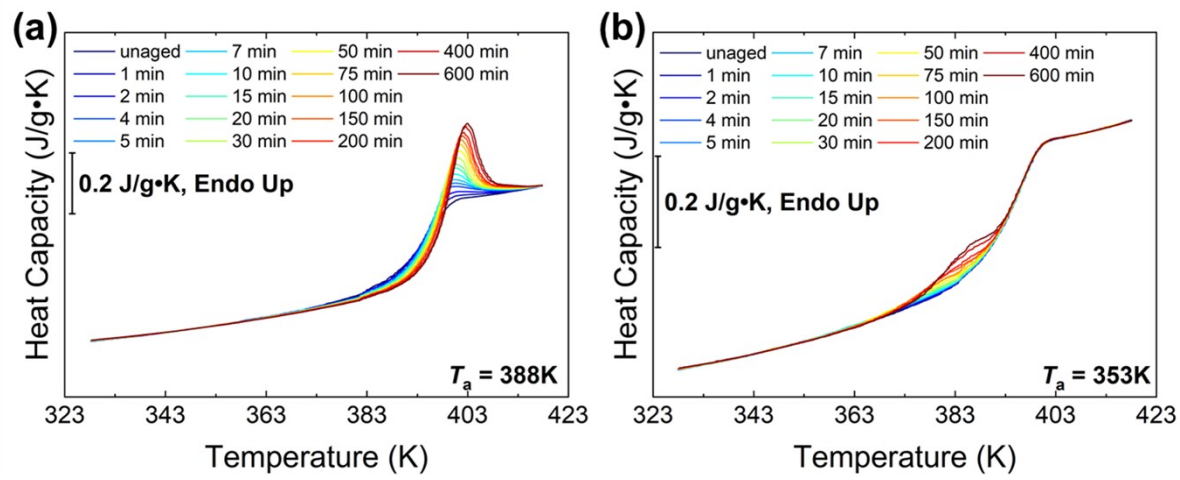

Figure 6. Re-heating thermograms after aging HPMCAS-HF at t_a for T_a = **(a)** 388K and **(b)** 353K.

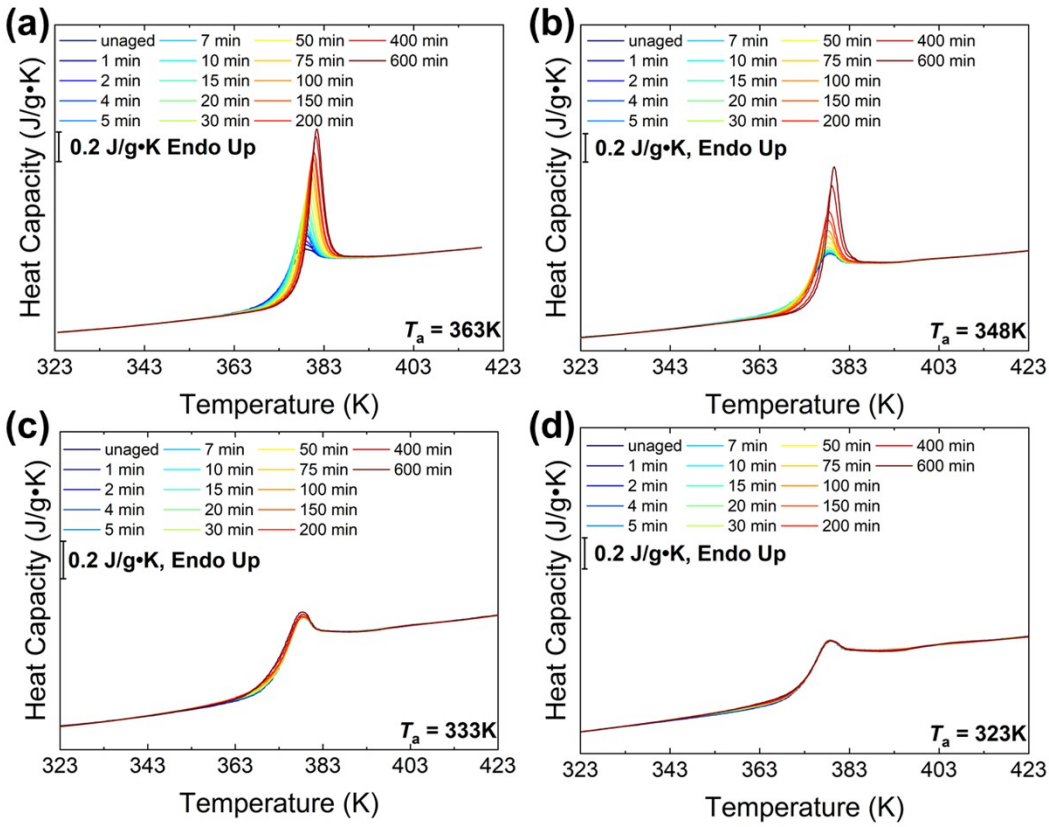

Figure 7. Re-heating thermograms after aging PS (MW=16 kg/mol) at t_a for T_a = **(a)** 363K, **(b)** 348K, **(c)** 333K, and **(d)** 323K.

Aging Temperature (K)	Range of Fit (min)	Aging Rate (K/$\log_{10}$(min))	R-square Value
313	2 – 600	0.90±0.02	0.991
323	2 – 600	0.74±0.01	0.995
333	2 – 600	0.77±0.02	0.994
343	10 – 600	0.83±0.02	0.994
353	20 – 600	1.03±0.02	0.998
363	10 – 600	0.95±0.02	0.995
373	5 – 150	1.08±0.07	0.971
383	2 – 150	0.97±0.06	0.965
388	1 – 20	1.08±0.08	0.967

Table 2. Range of linear fit for all T_a in this study. The best fits were determined by selecting the fit that yielded an R-square value closest to unity or greater than 0.96.

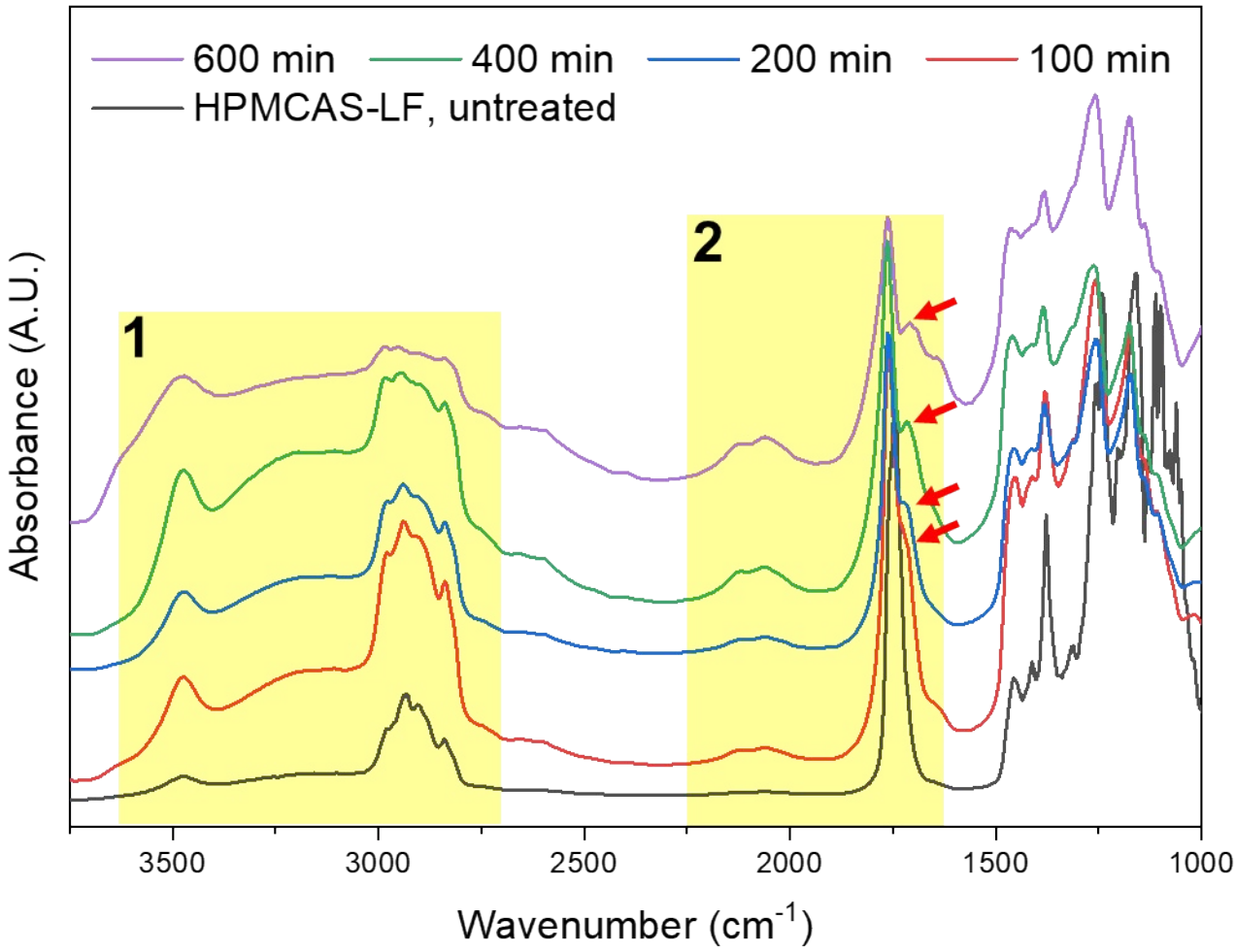

Figure 8. FTIR spectra of untreated HPMCAS-LF and HPMCAS-LF aged at T_a = 353K for 100, 200, 400, and 600 minutes. The data were vertically translated for visual clarity. This data is near identical to that shown in Figure 8a of the main text.

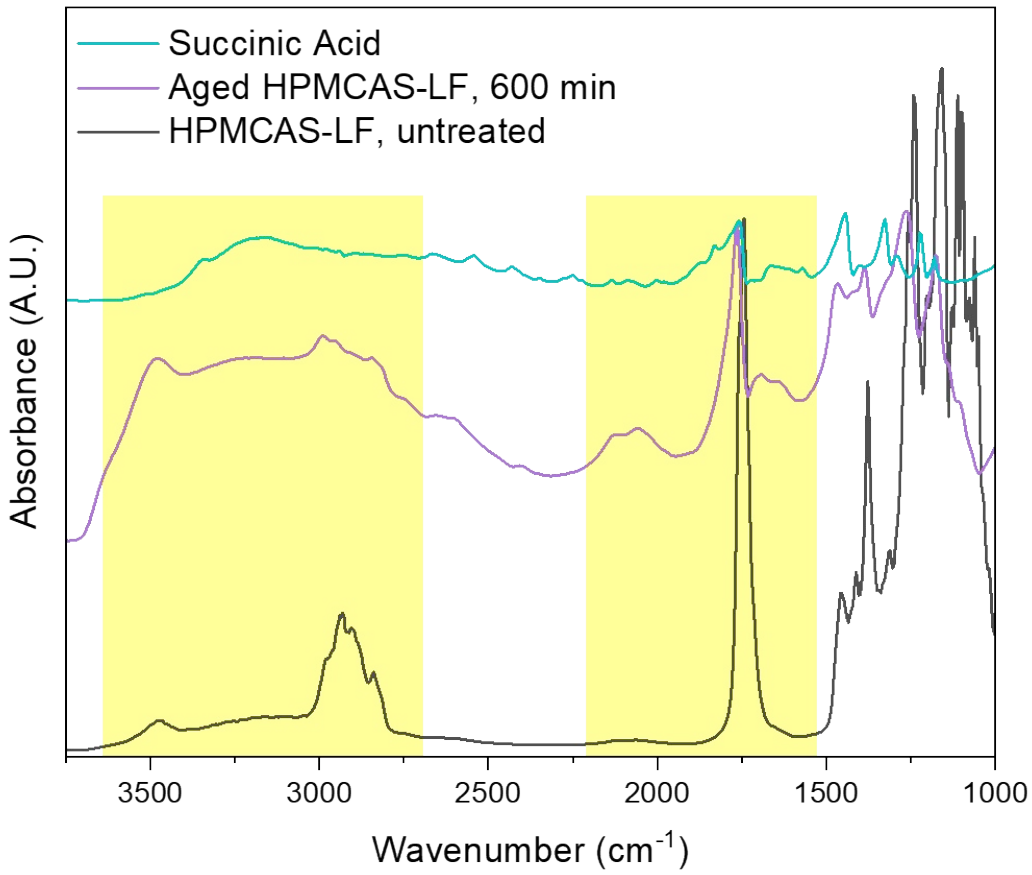

Figure 9. FTIR data of succinic acid (as received), the HPMCAS-LF aged at 388K for 600 min, and the untreated HPMCAS-LF. The primary two regions discussed in the main text is highlighted. The FTIR spectra of aged HPMCAS-LF and the succinic acid share the broad peak near 3250 cm^{-1} and the shoulder peak near 1750 cm^{-1}.