Rheology and Nanostructure of Hydroxypropyl Methylcellulose at High-Shear Rates

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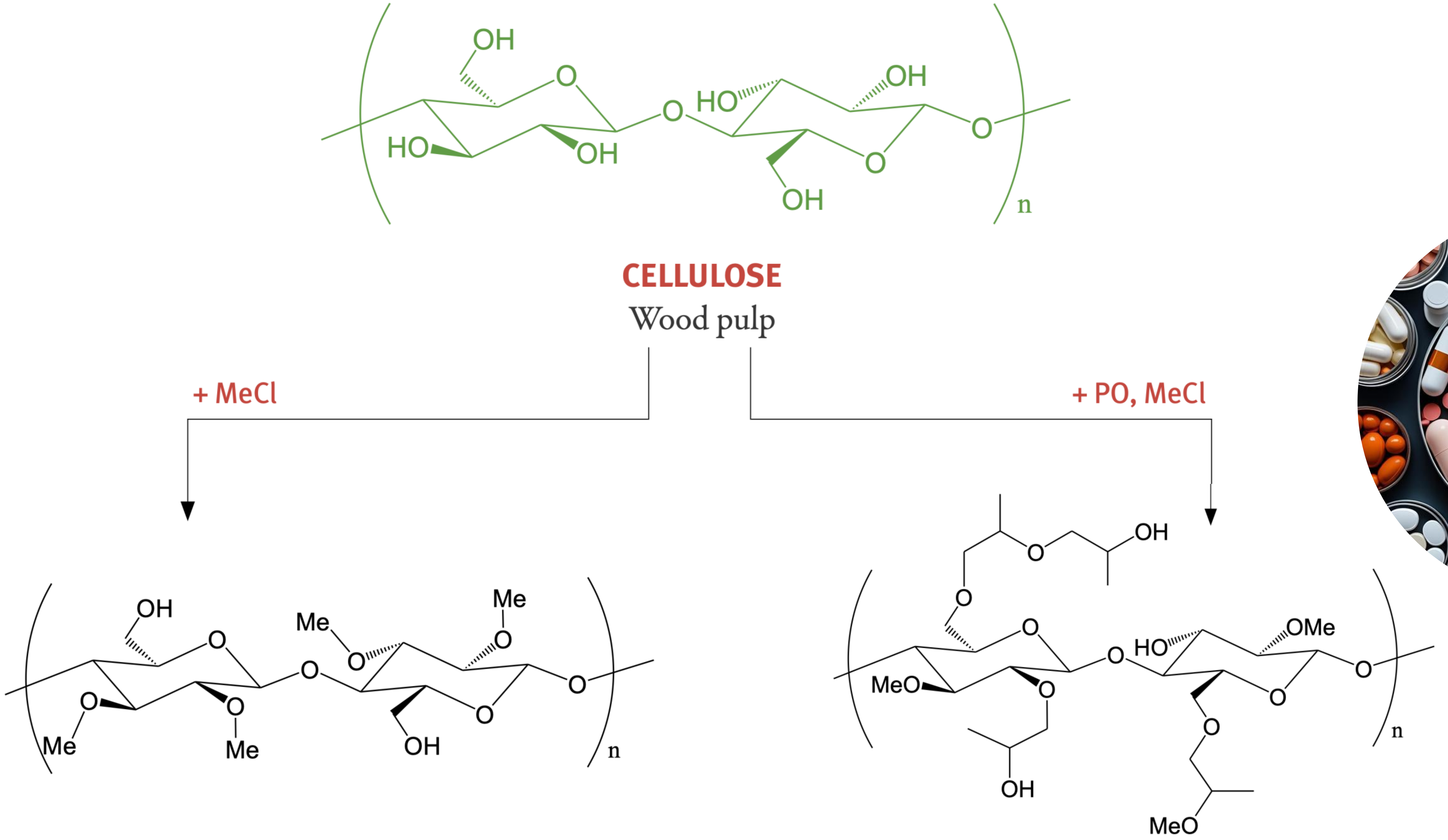
Hydroxypropyl Methylcellulose (HPMC)



METHOCEL™ A
(Methylcellulose / MC)

METHOCEL™ E,F,K,J
(Hydroxypropyl Methylcellulose / HPMC)

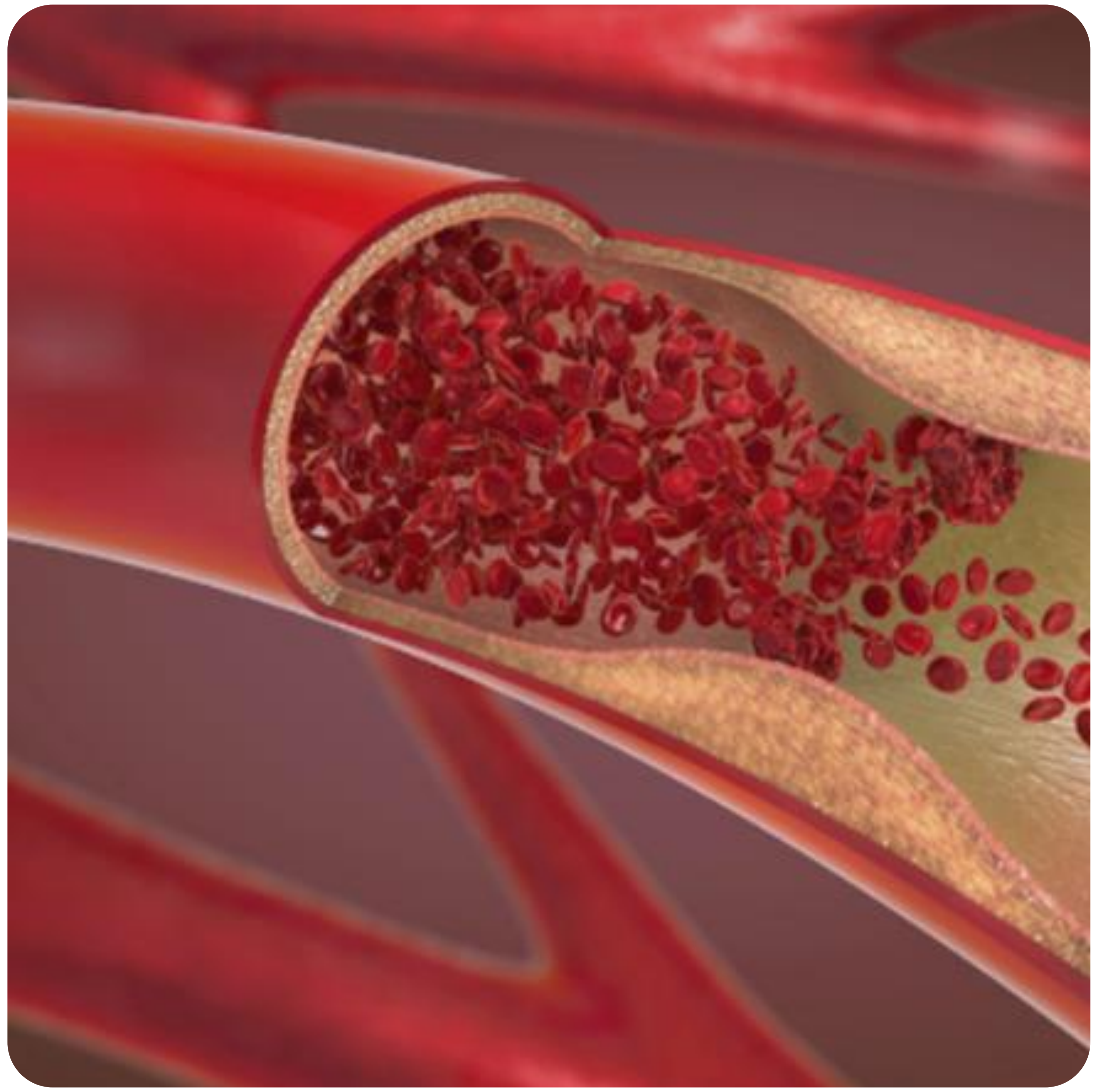




DuPont (2019). *Water-Soluble Cellulosic Polymers for Industrial Applications.*

HPMC experiences high-shear rates in various applications

Pharmaceuticals



Blood Flow:

$\dot{\gamma} \approx 10^3 - 10^4\ s^{-1}$

Surfactants & Coatings

Spraying:

$\dot{\gamma} \approx 10^3 - 10^5\ s^{-1}$

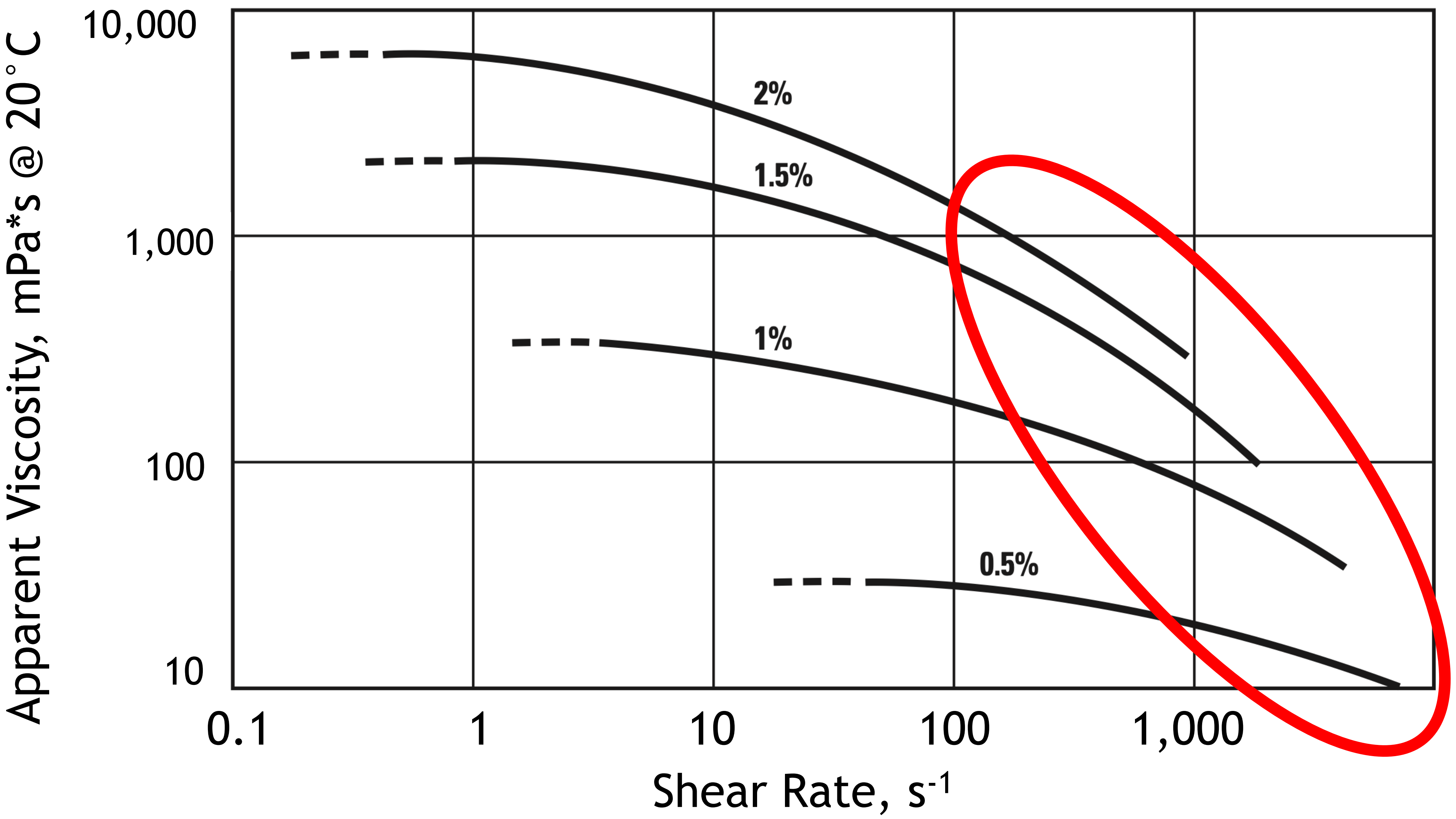
Lubricants

Lubrication:

$\dot{\gamma} \approx 10^5 - 10^7\ s^{-1}$

Does HPMC continue shear thinning at high-shear rates?

Sample	Mn (kg/mol)	Methoxy %	Propylene oxide %	Zero-shear viscosity @ 2 wt%, 20C, lit (mPa-s)	Gel temp (C)
HPMC Mn-10,000	10	29%	7%	6	58-64
HPMC Mn-120,000	120	21%	5%	100000	70-90
HPMC Mn-90,000	90	21%	5%	15000	70-90
METHOCEL F50	20-26	27-30%	4-7%	50	50-70



Dow (2002). *METHOCEL Cellulose Ethers Technical Handbook*.

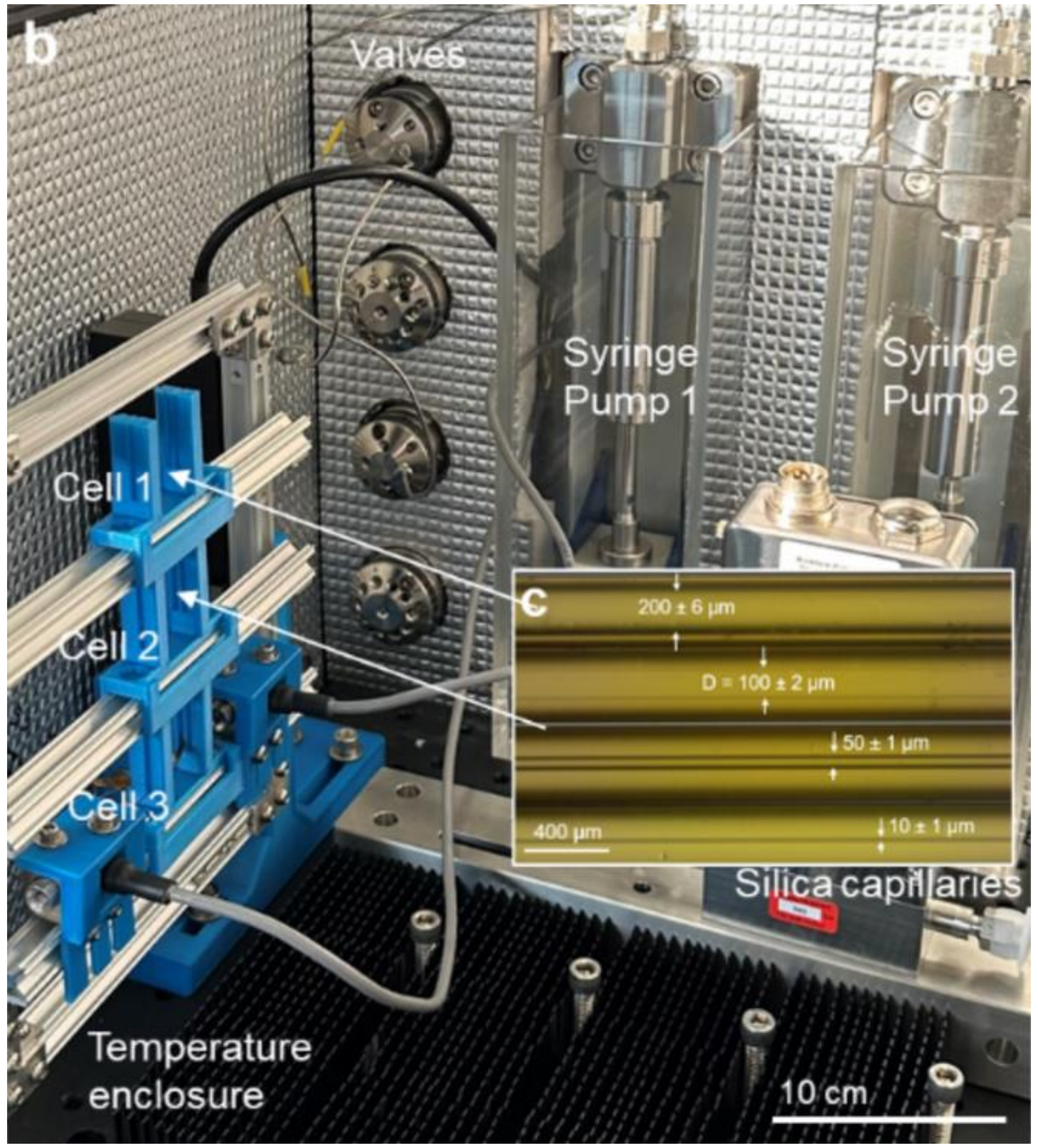
Rheology is used to determine HPMC behavior at a wide range of shear rates

Variables:

- Shear Rate
- Molecular Weight
- Degree of Substitution
- Concentration
- Temperature

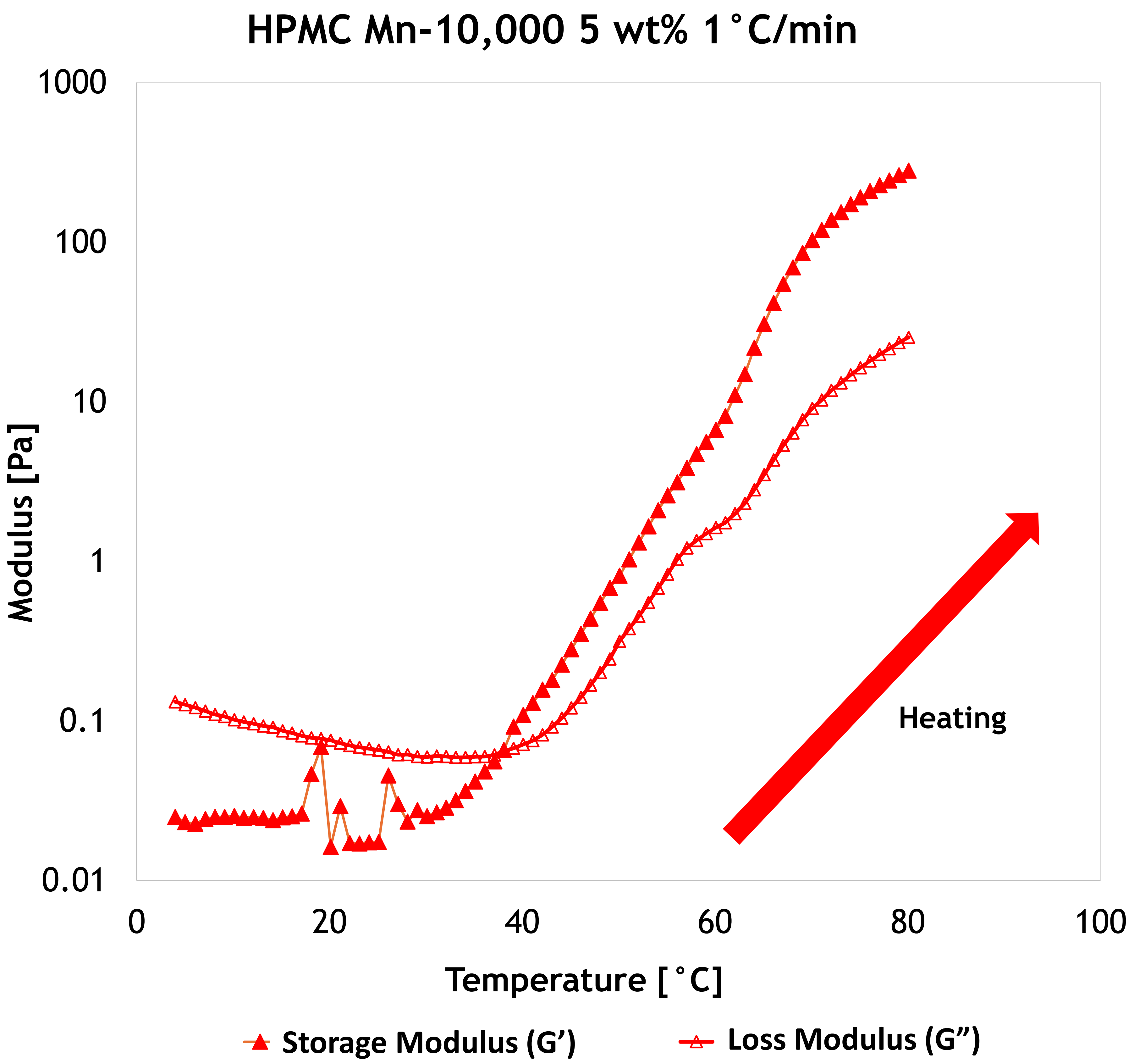
Rotational Rheometer

Capillary Rheometer

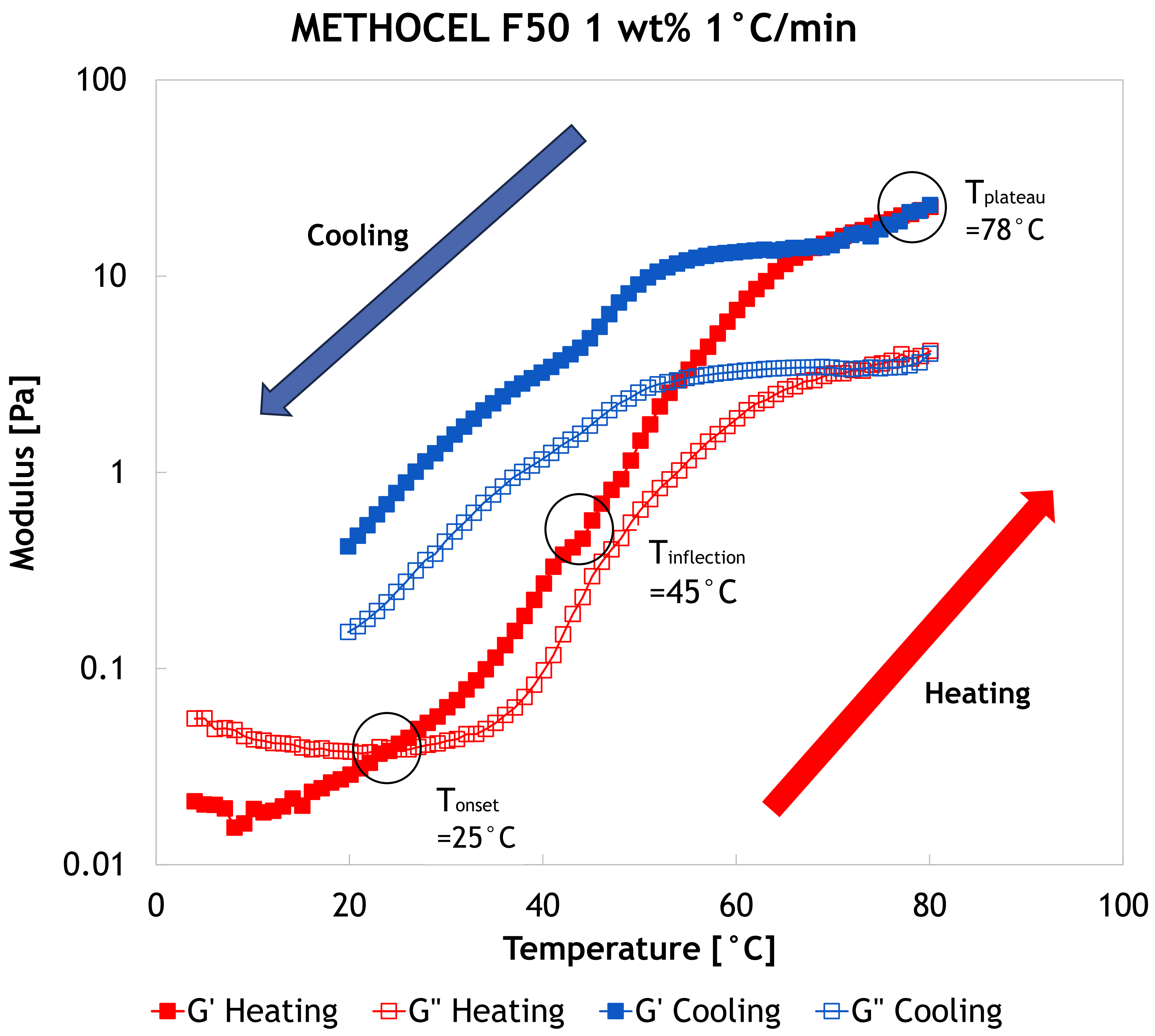


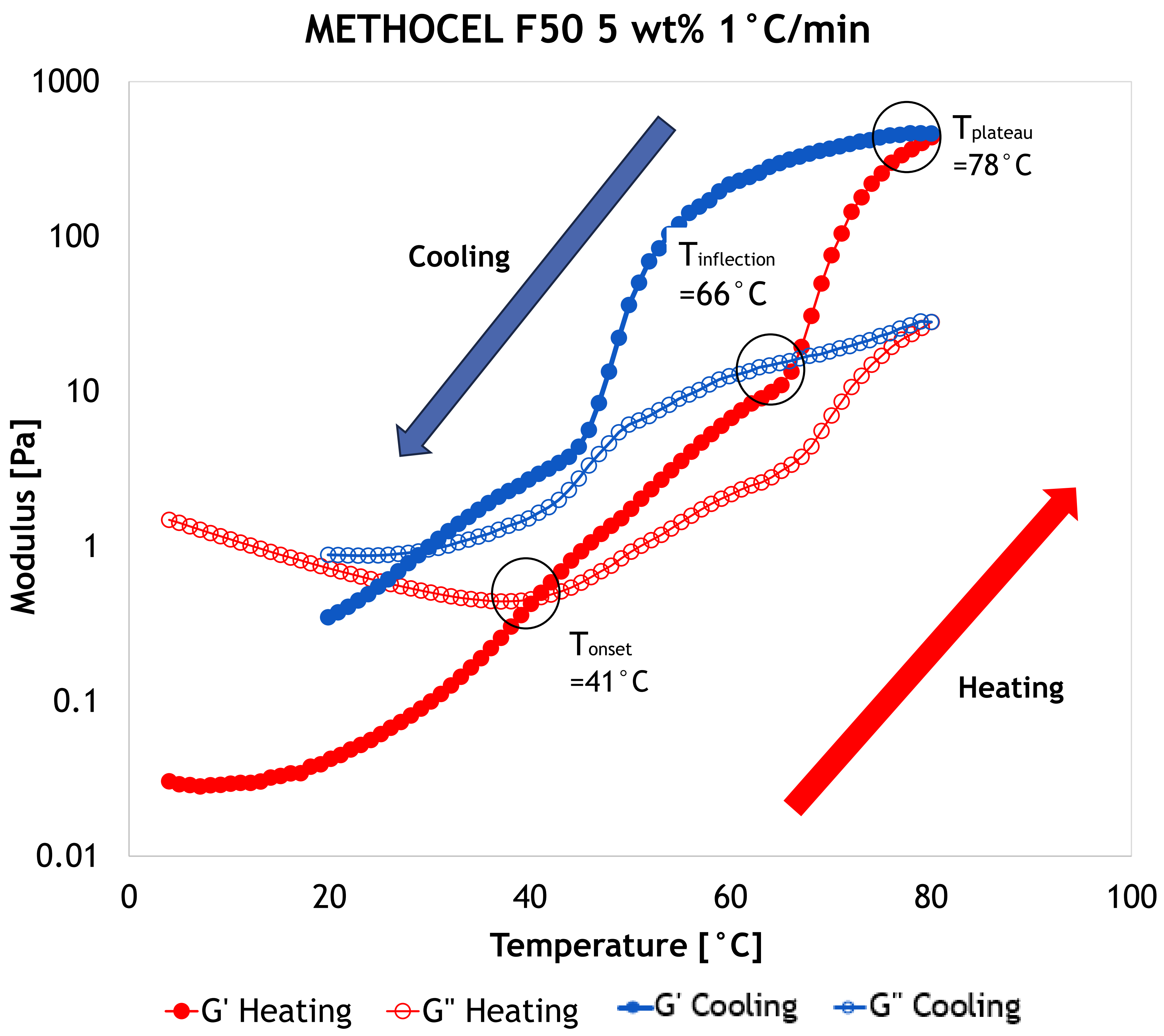
Murphy et al., *Soft Matter* (2020). Capillary RheoSANS: measuring the rheology and nanostructure of complex fluids at high shear rates.

Gelation occurs over a broad temperature range

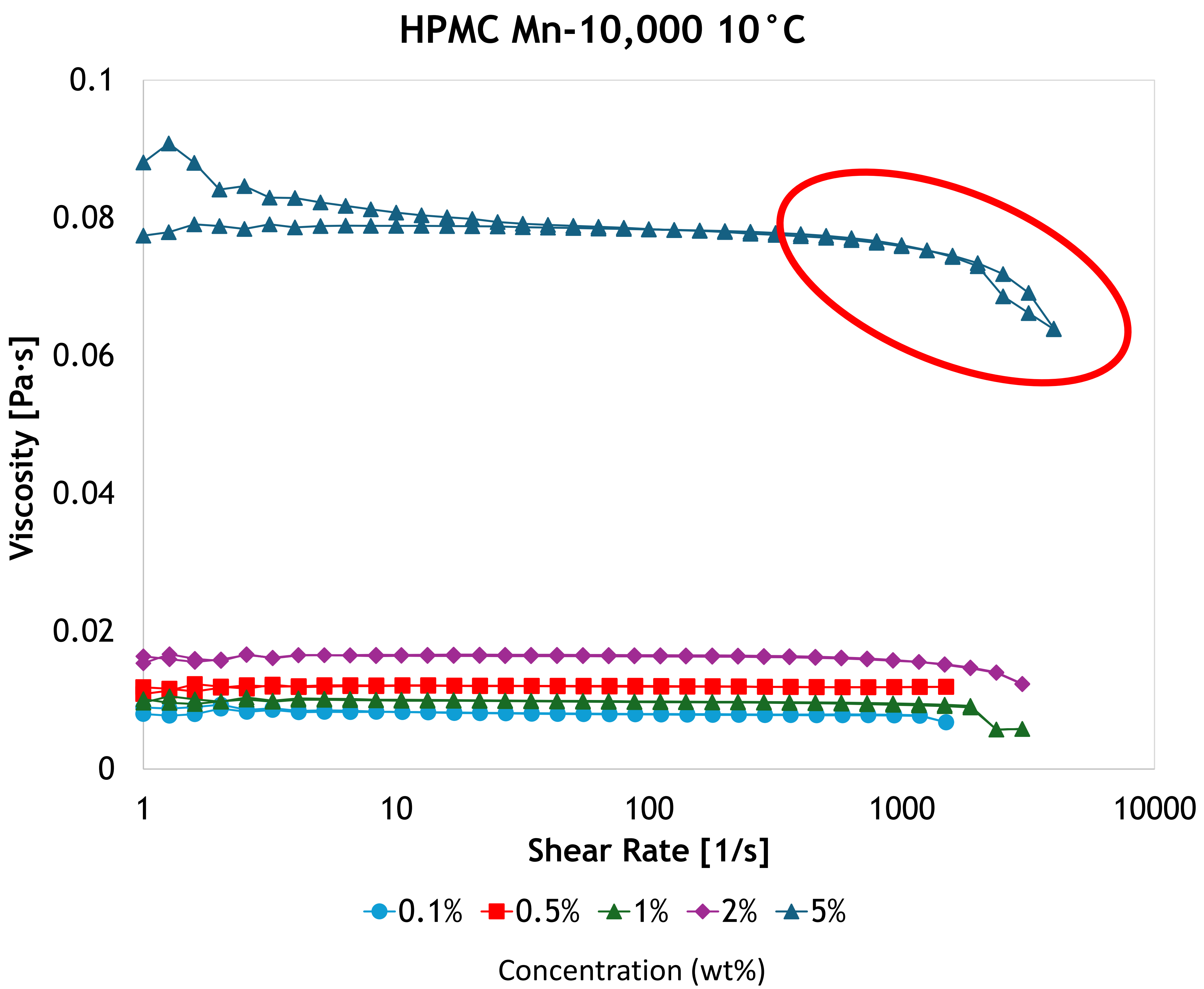


Gelation occurs over a broad temperature range

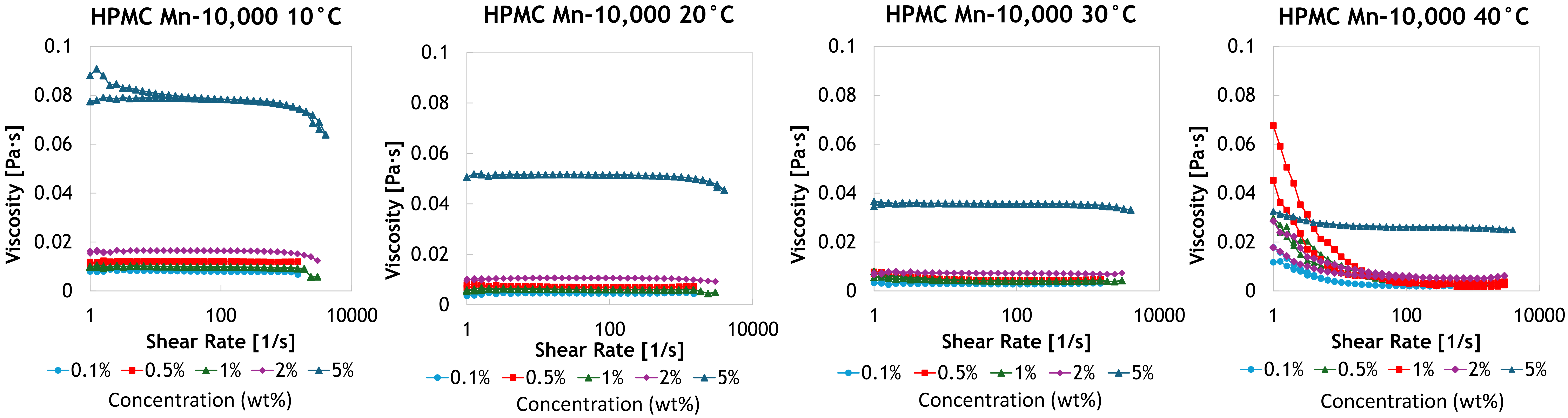




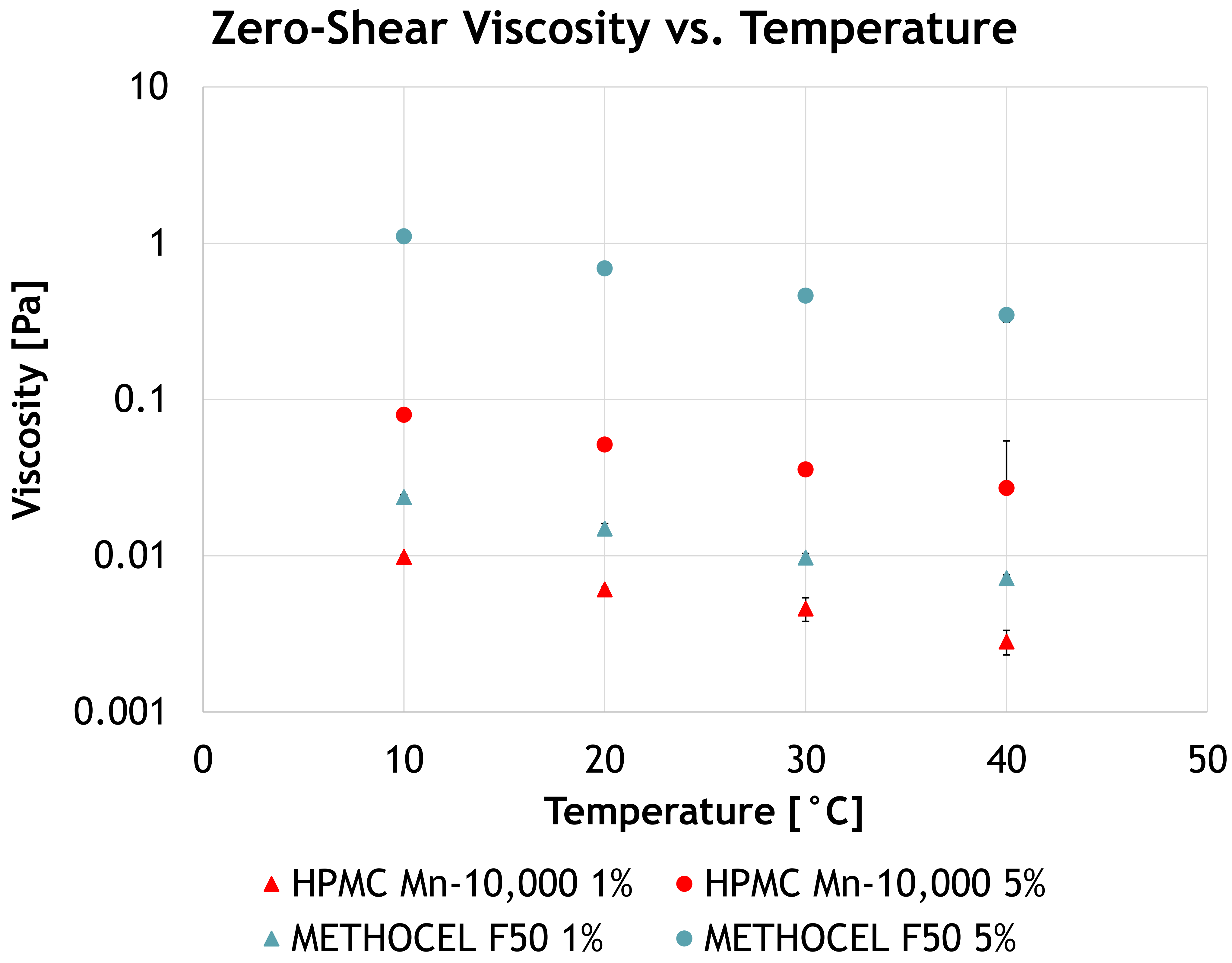
Shear thinning starts occurring at low-shear rates



Viscosity decreases as temperature increases from 10°C to 40°C



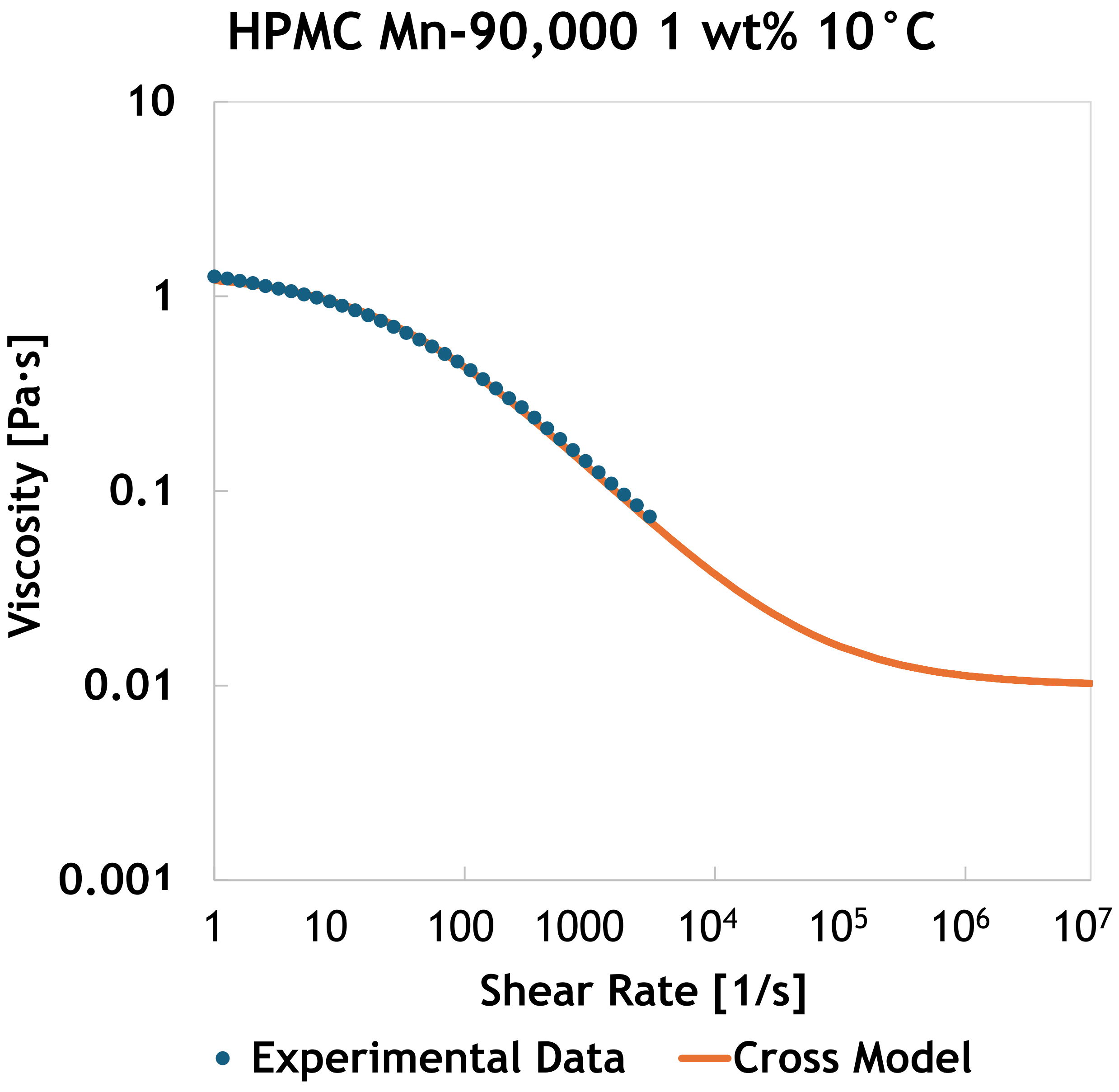
Zero-shear viscosity helps to predict high-shear behavior

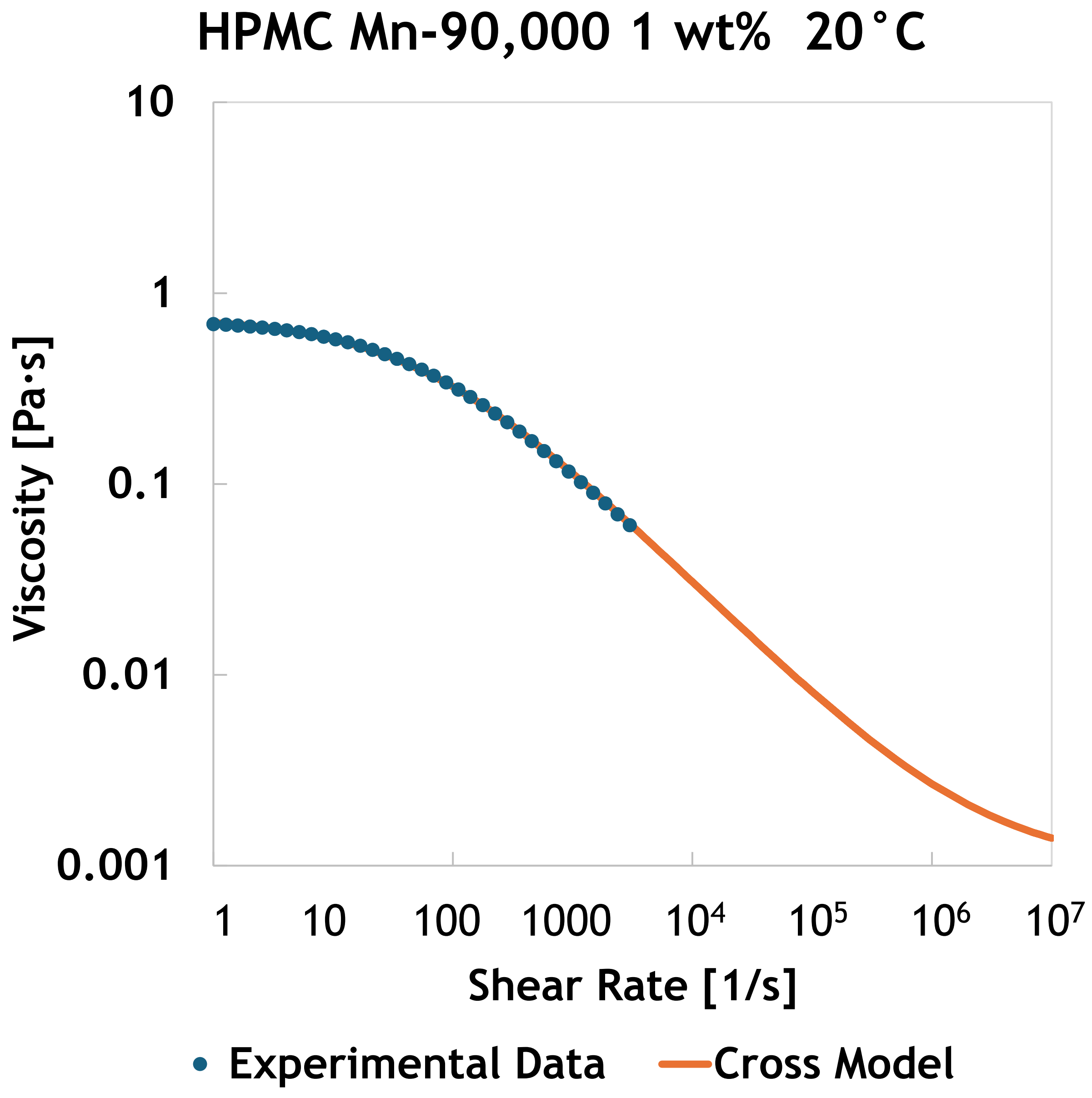


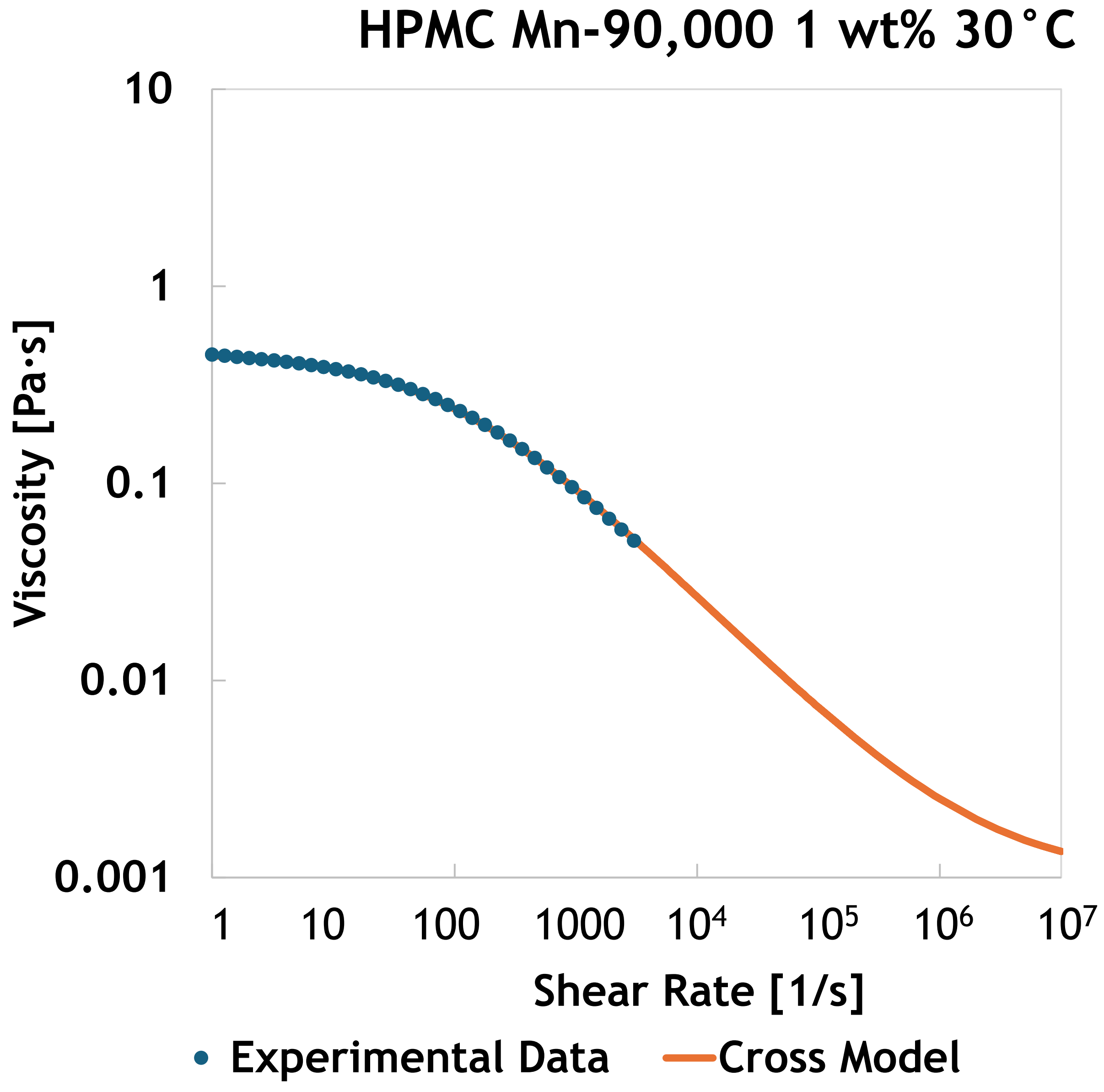
Note: Some zero-shear viscosities ignore yield stress at low-shear rates

Predicting high-shear behavior: Cross Model

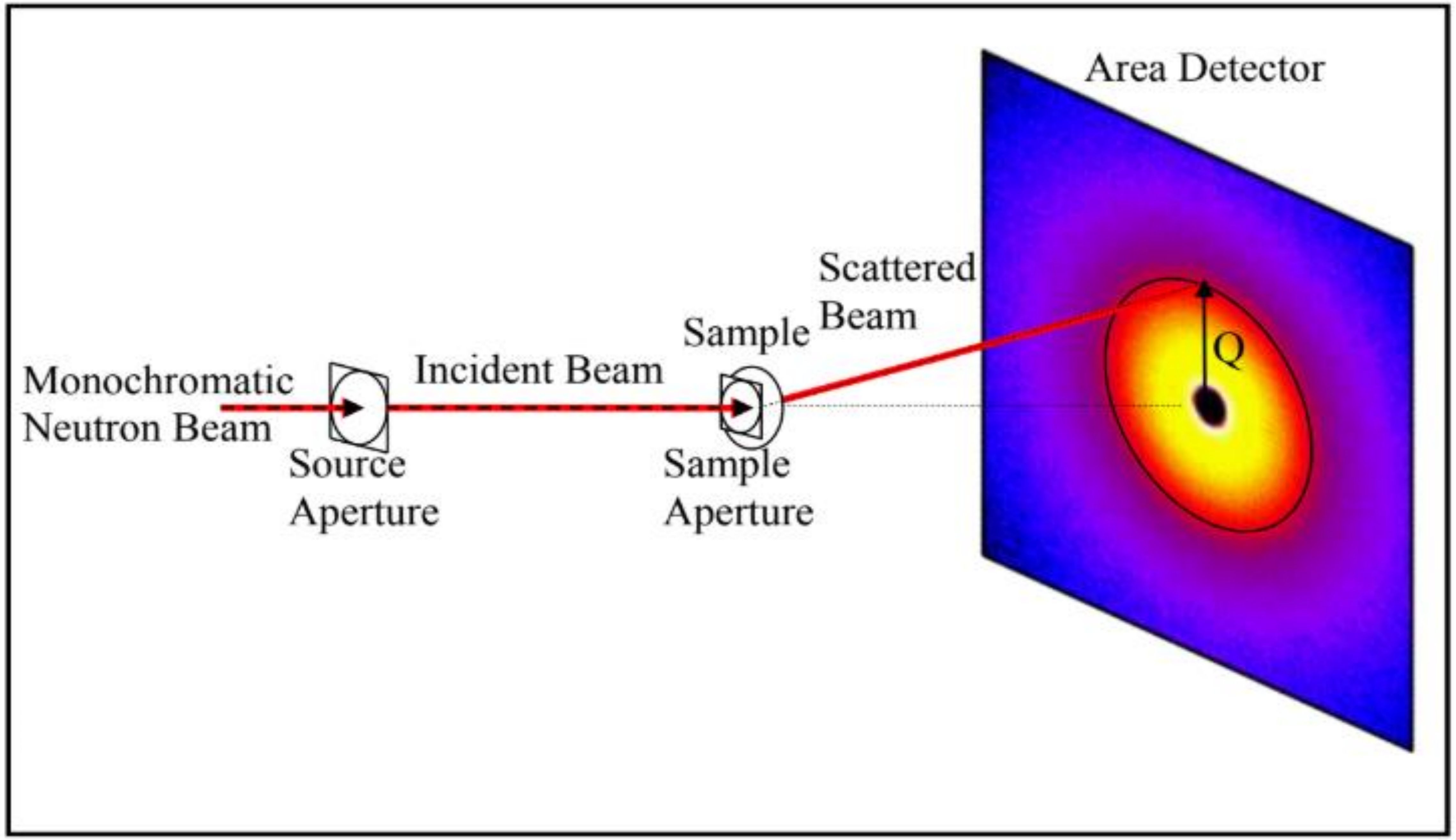
$$\eta = \eta_{inf} + \frac{\eta_0 - \eta_{inf}}{1+(\alpha\dot{\gamma})^n}$$





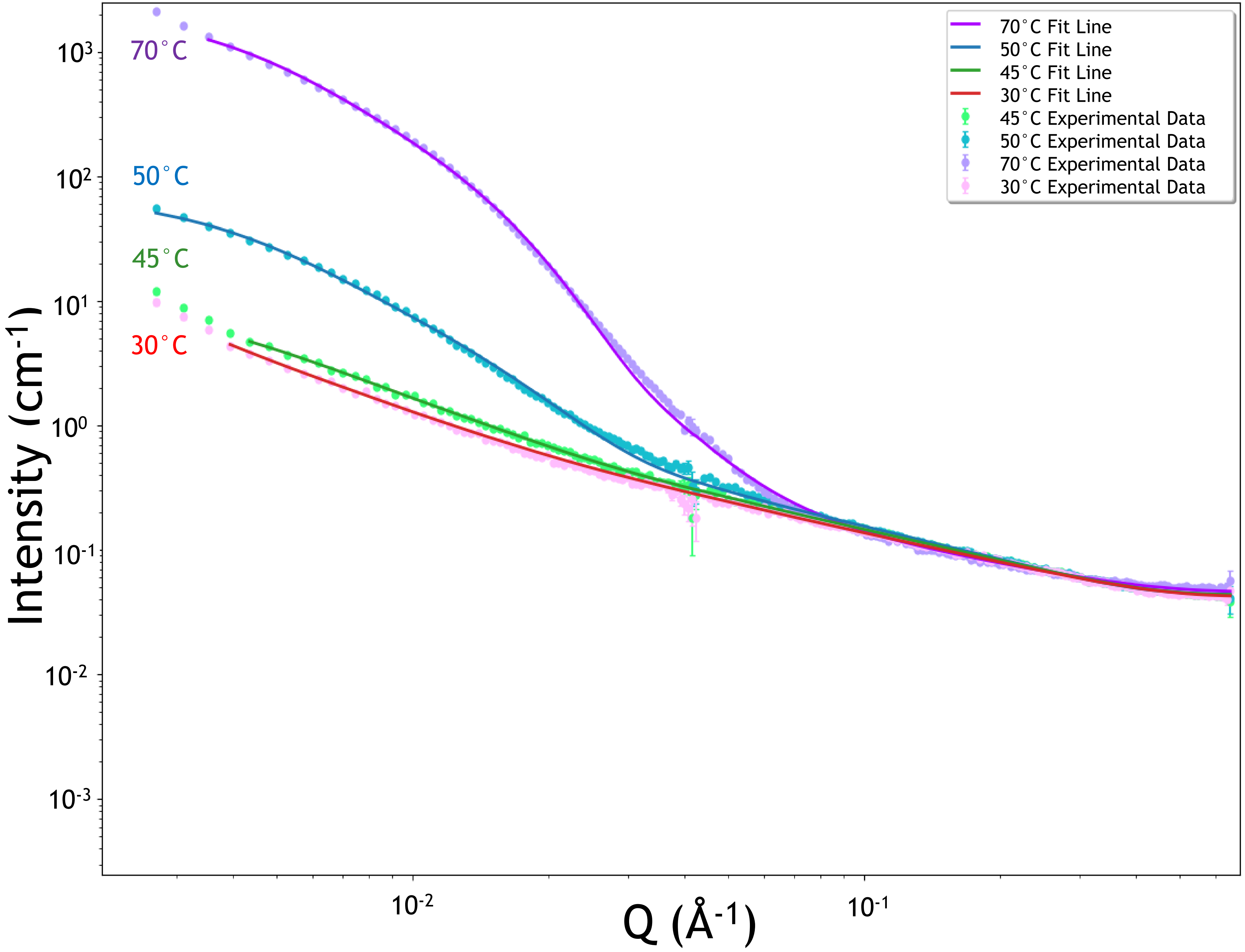


What is Small-Angle Neutron Scattering (SANS)?

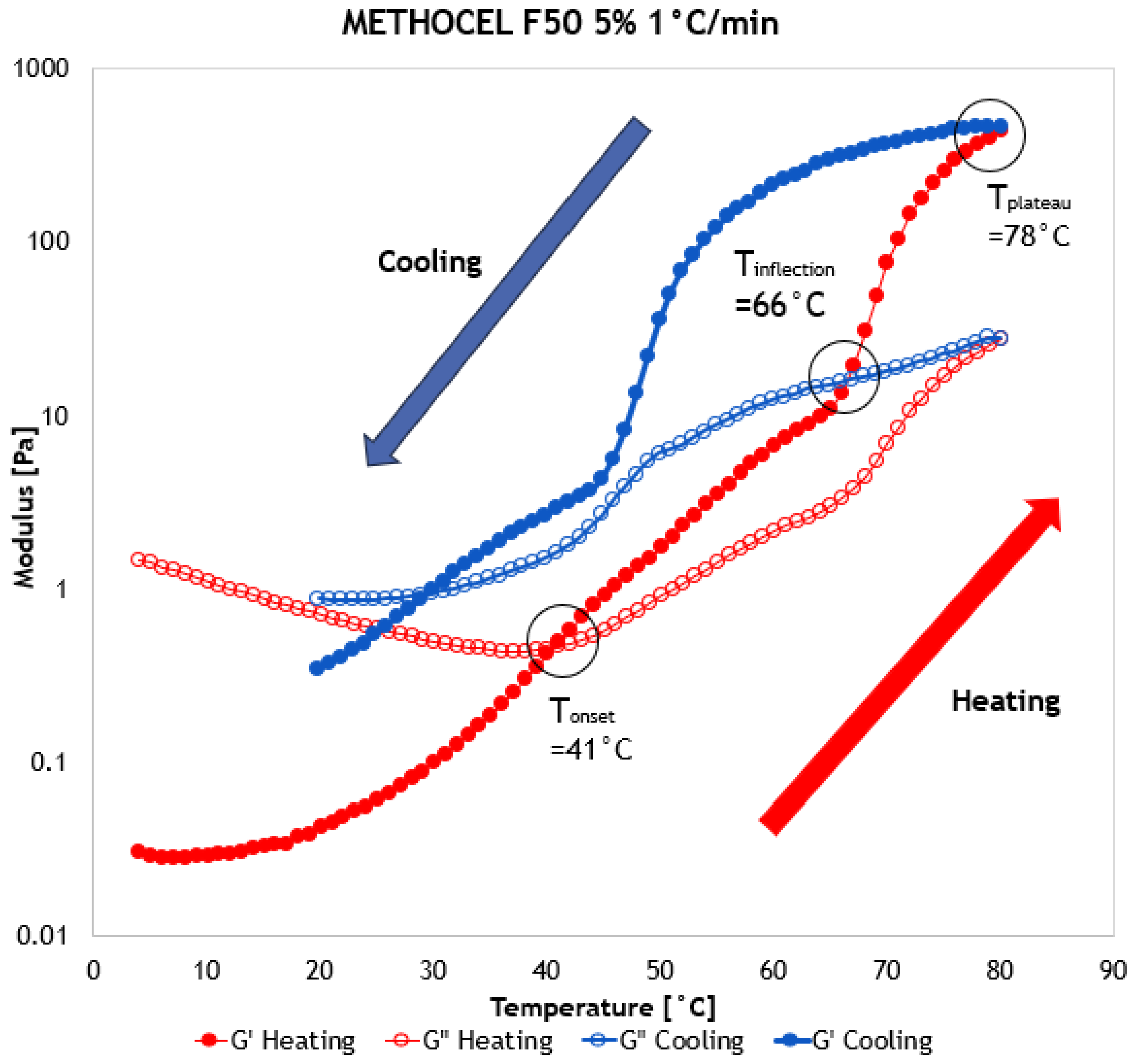


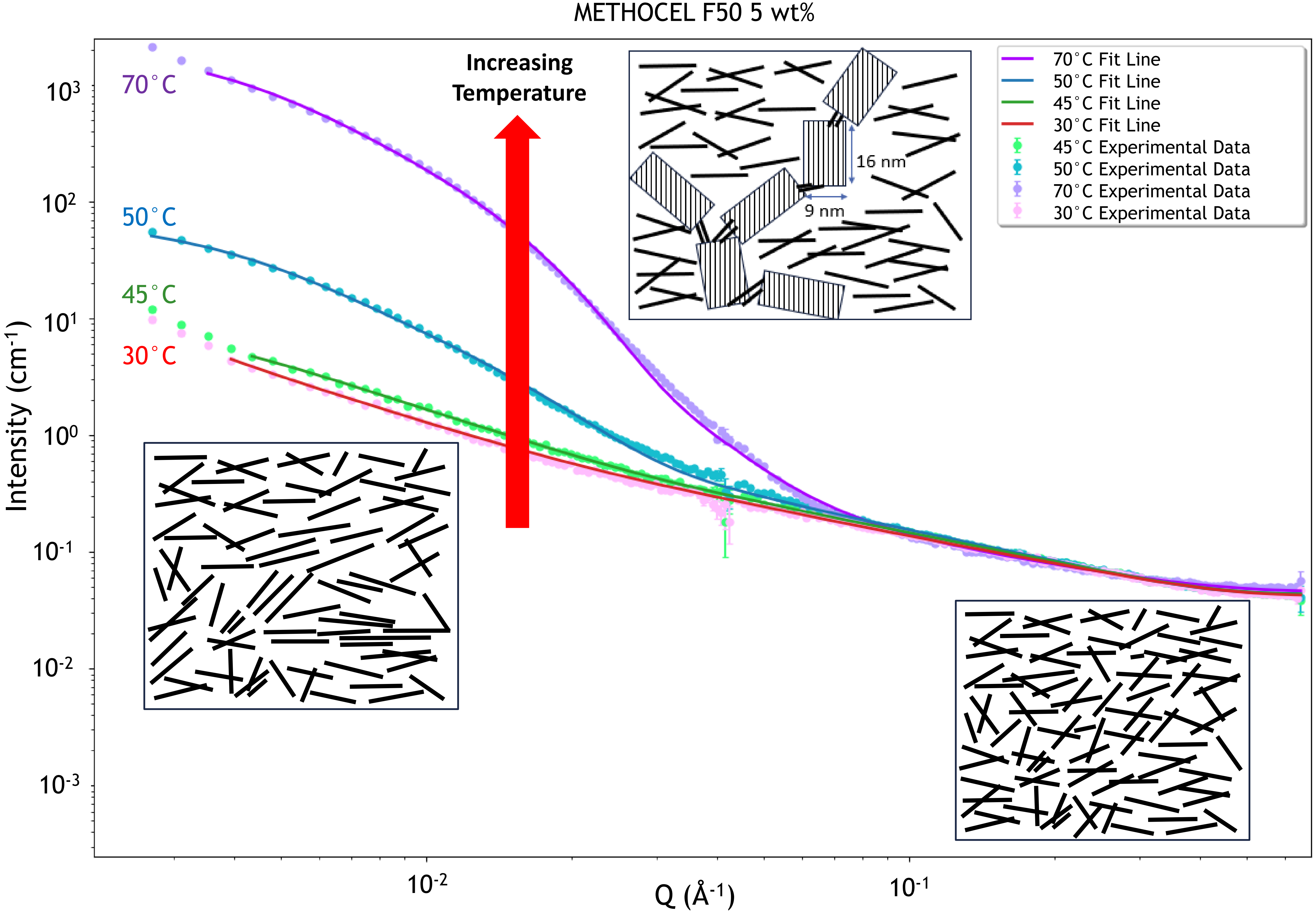
Hammouda (2016). *The SANS Toolbox*.

Determining nanostructure from SANS fitting

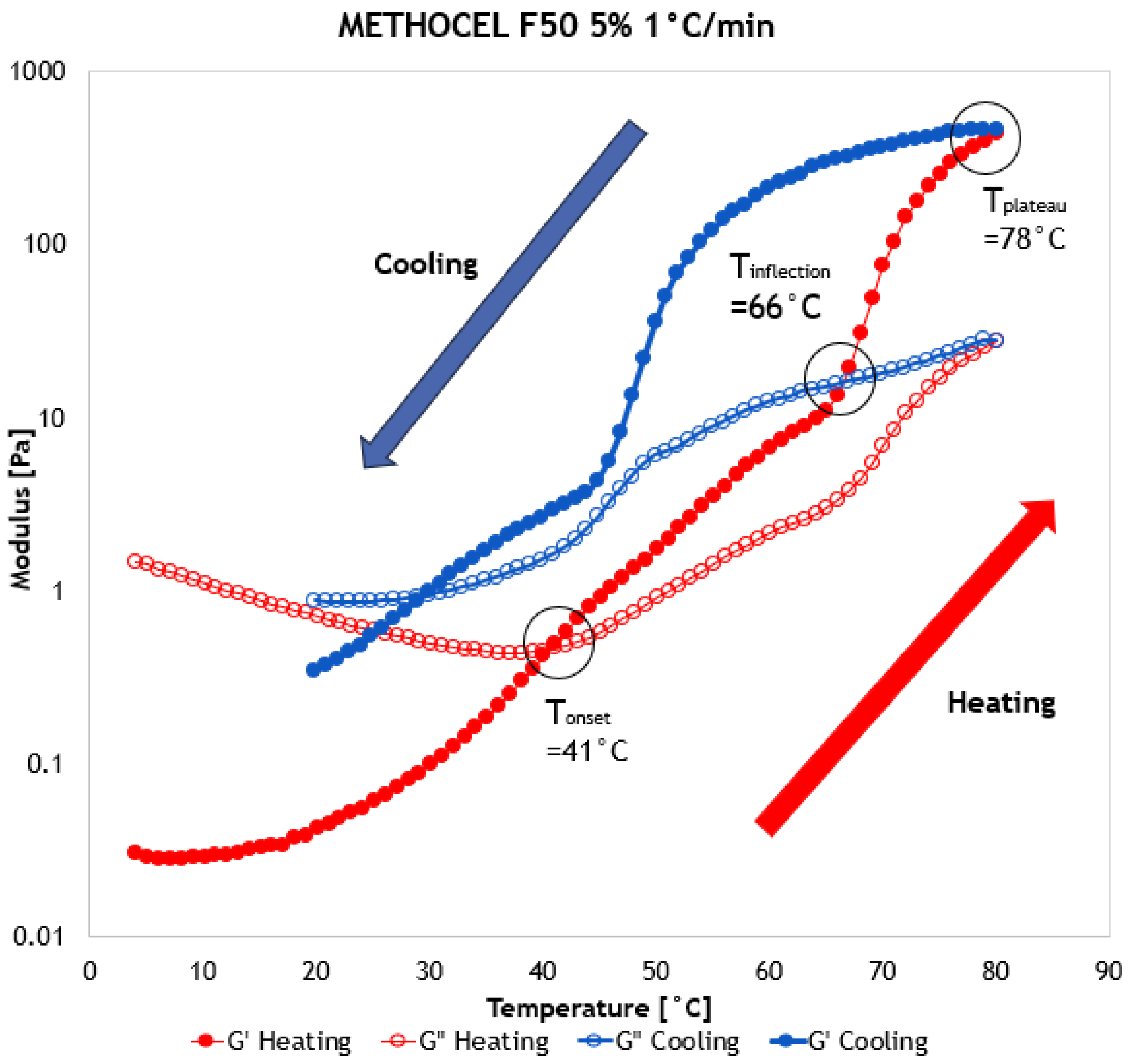


Determining nanostructure from SANS fitting

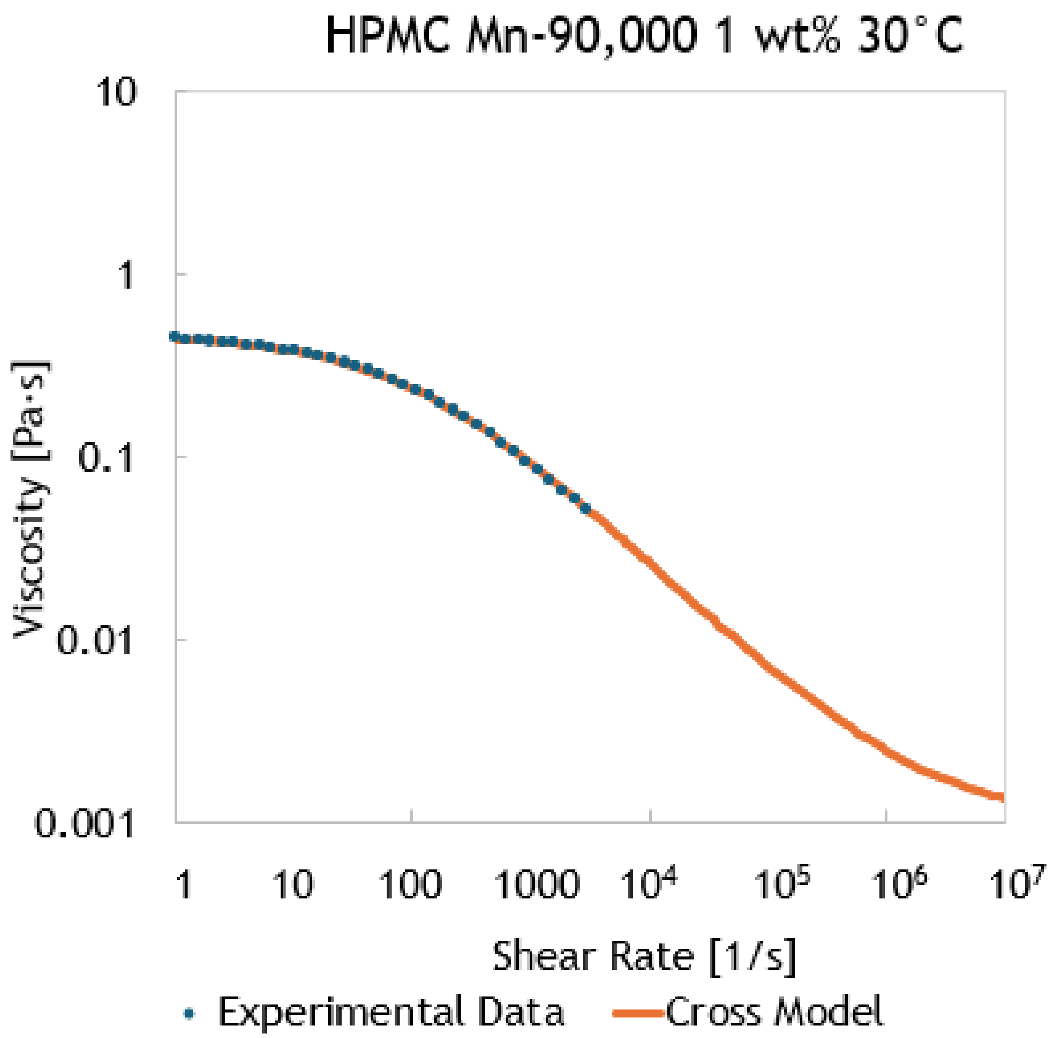




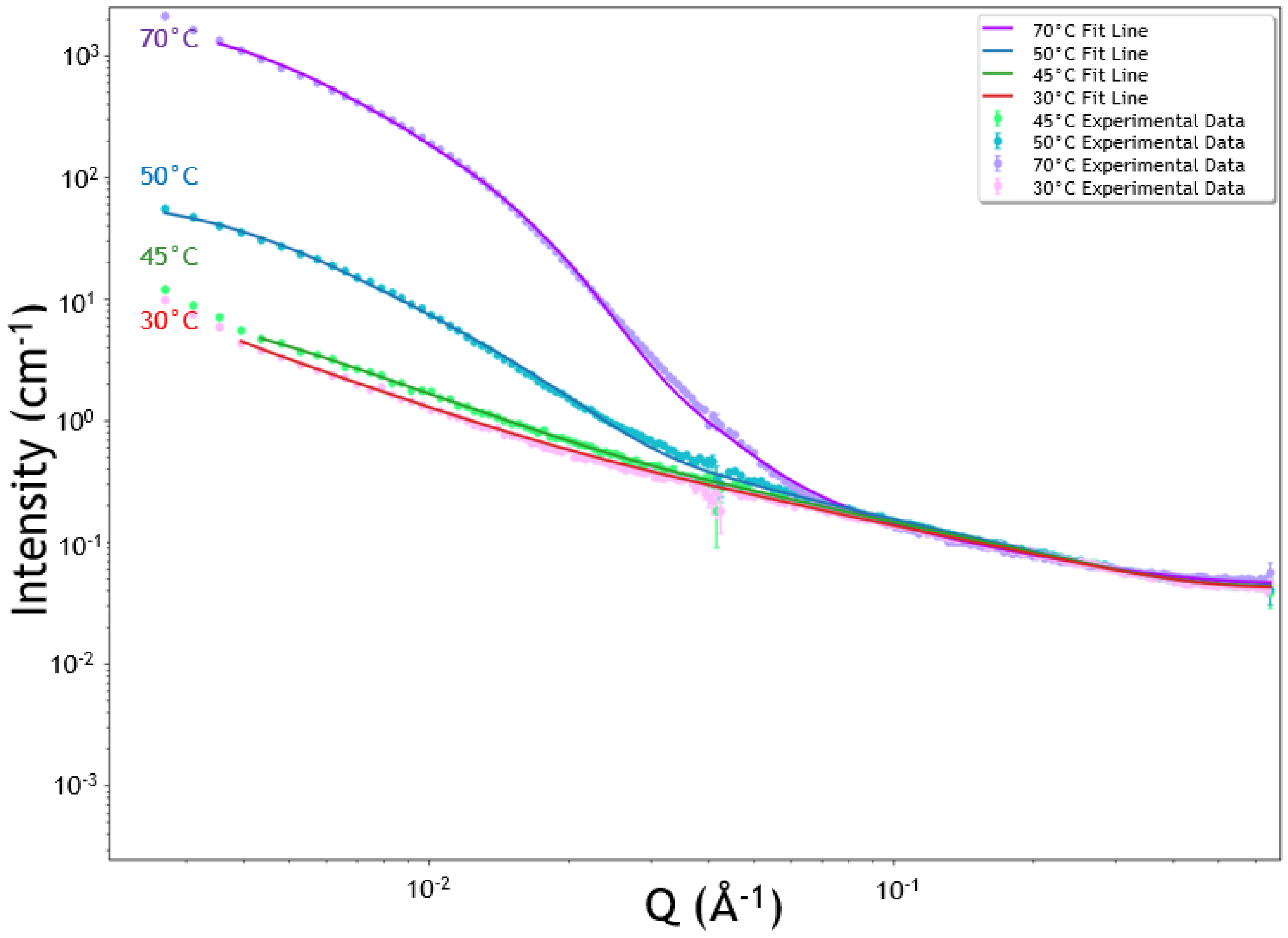
Gelation Temperature and Low-Shear Behavior



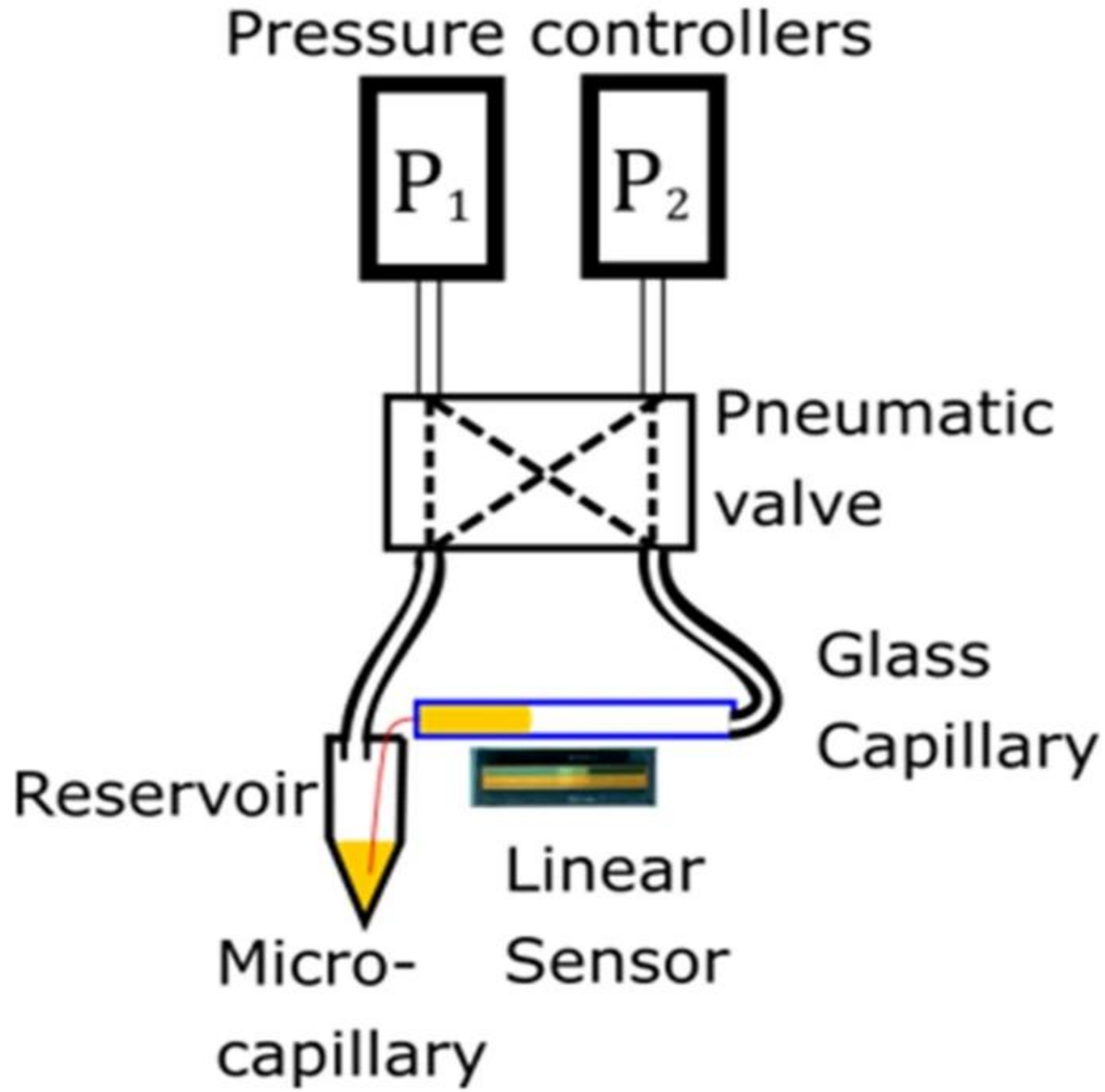
Predicting High-Shear Behavior

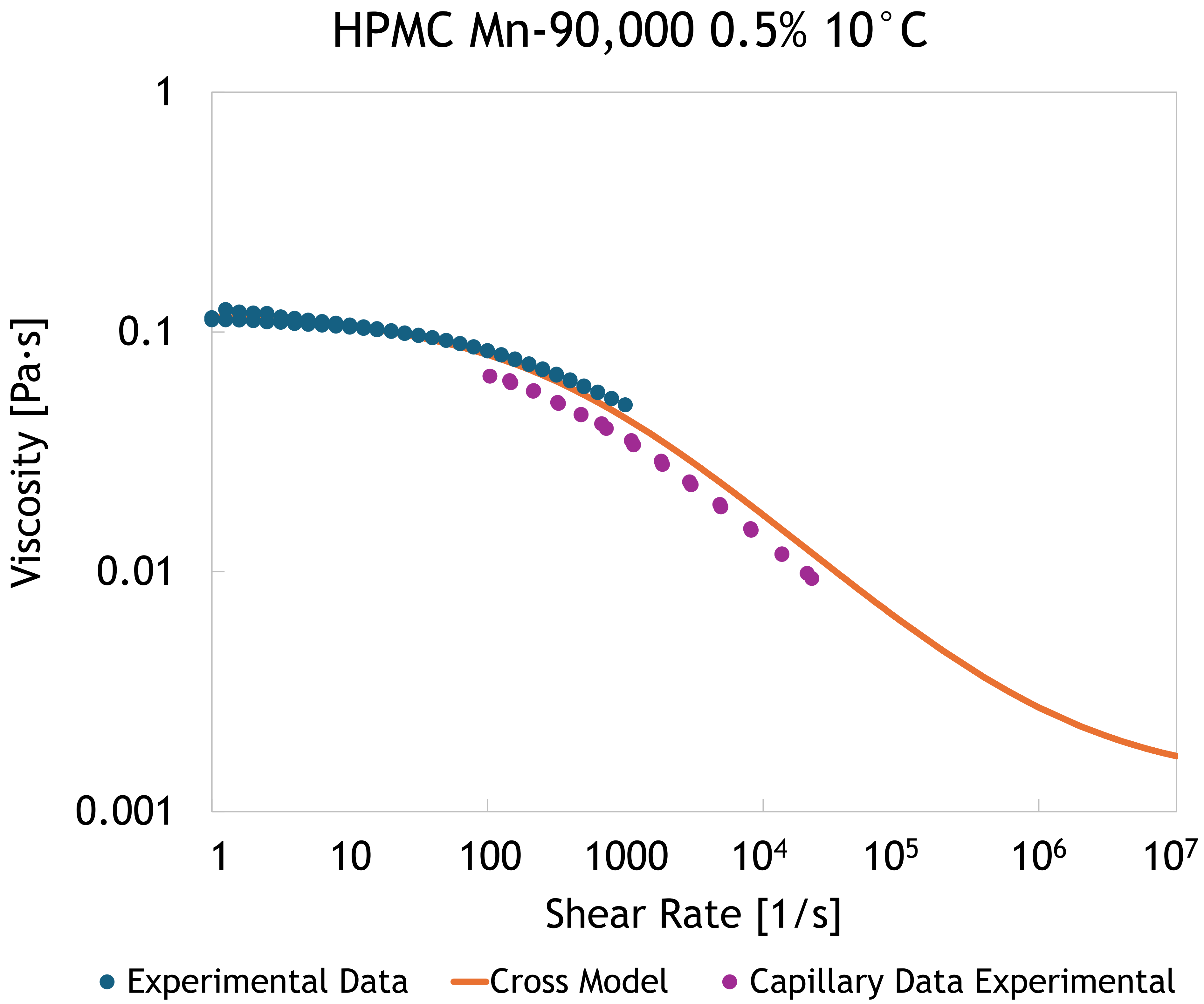


SANS Fitting and Nanostructure



Preliminary Results and Future Work





Murphy et al., *Soft Matter* (2020). Capillary RheoSANS: measuring the rheology and nanostructure of complex fluids at high shear rates.

Salipante et al., Rheologica Acta (2022). A small-volume microcapillary rheometer.

Acknowledgements

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Dr. Steven Hudson

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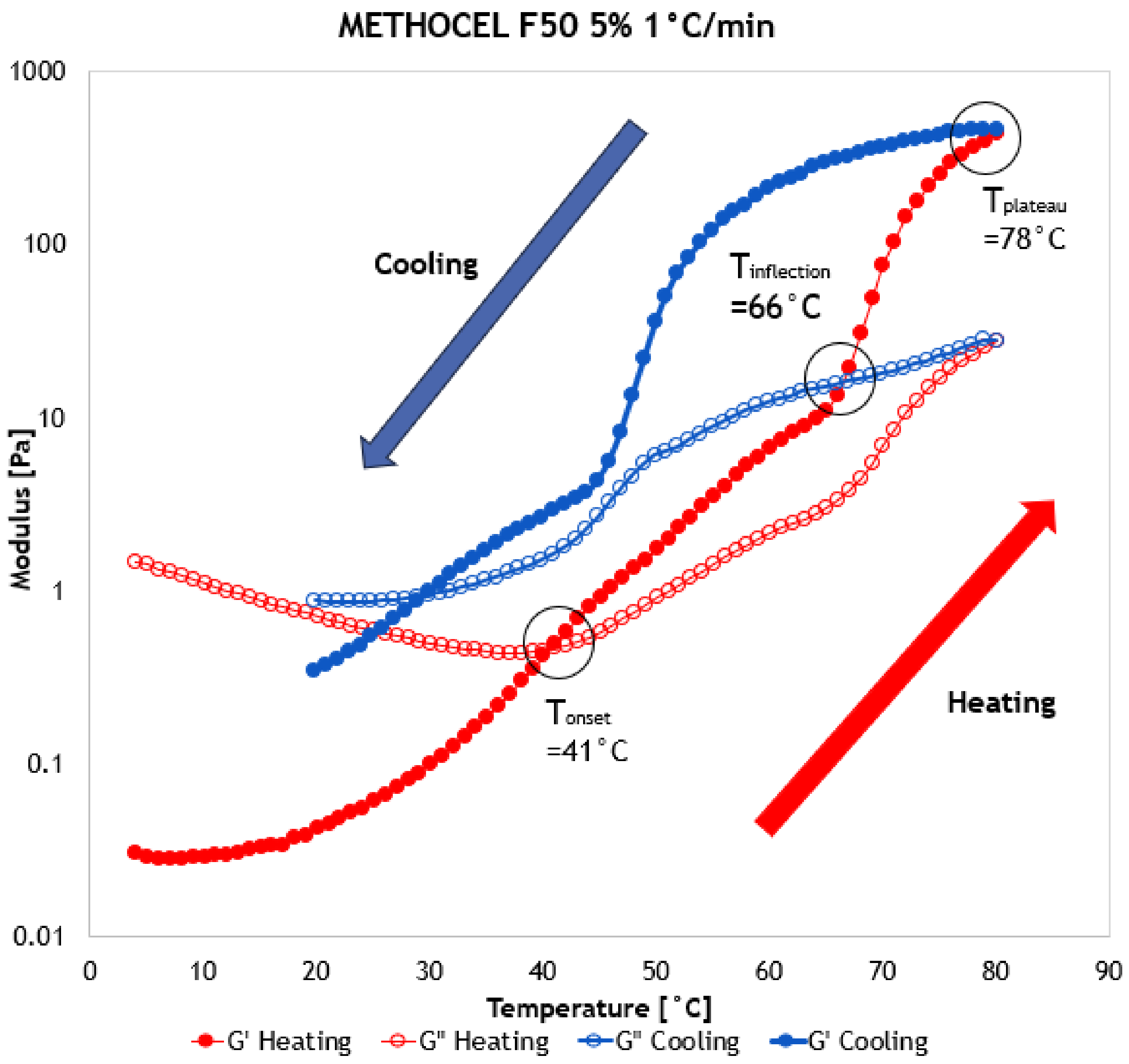
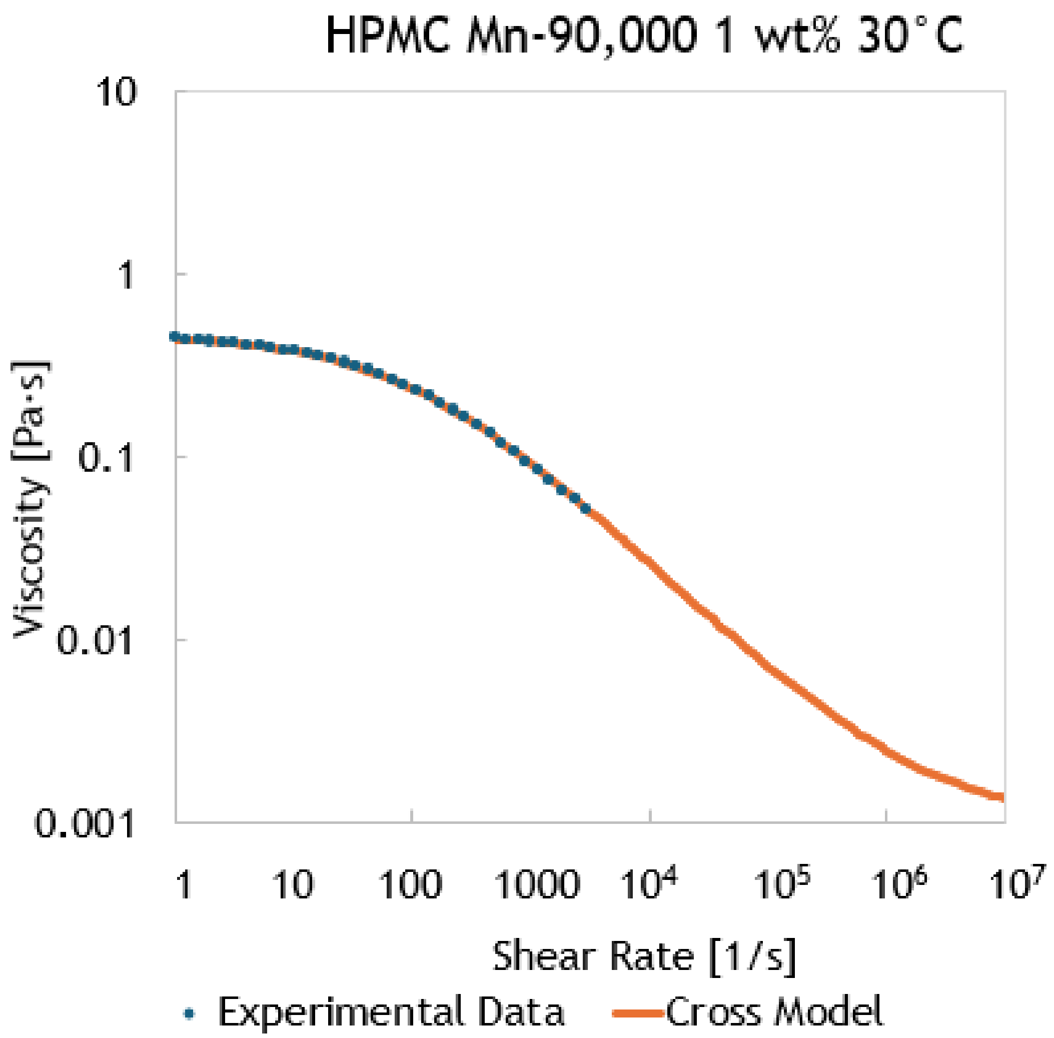
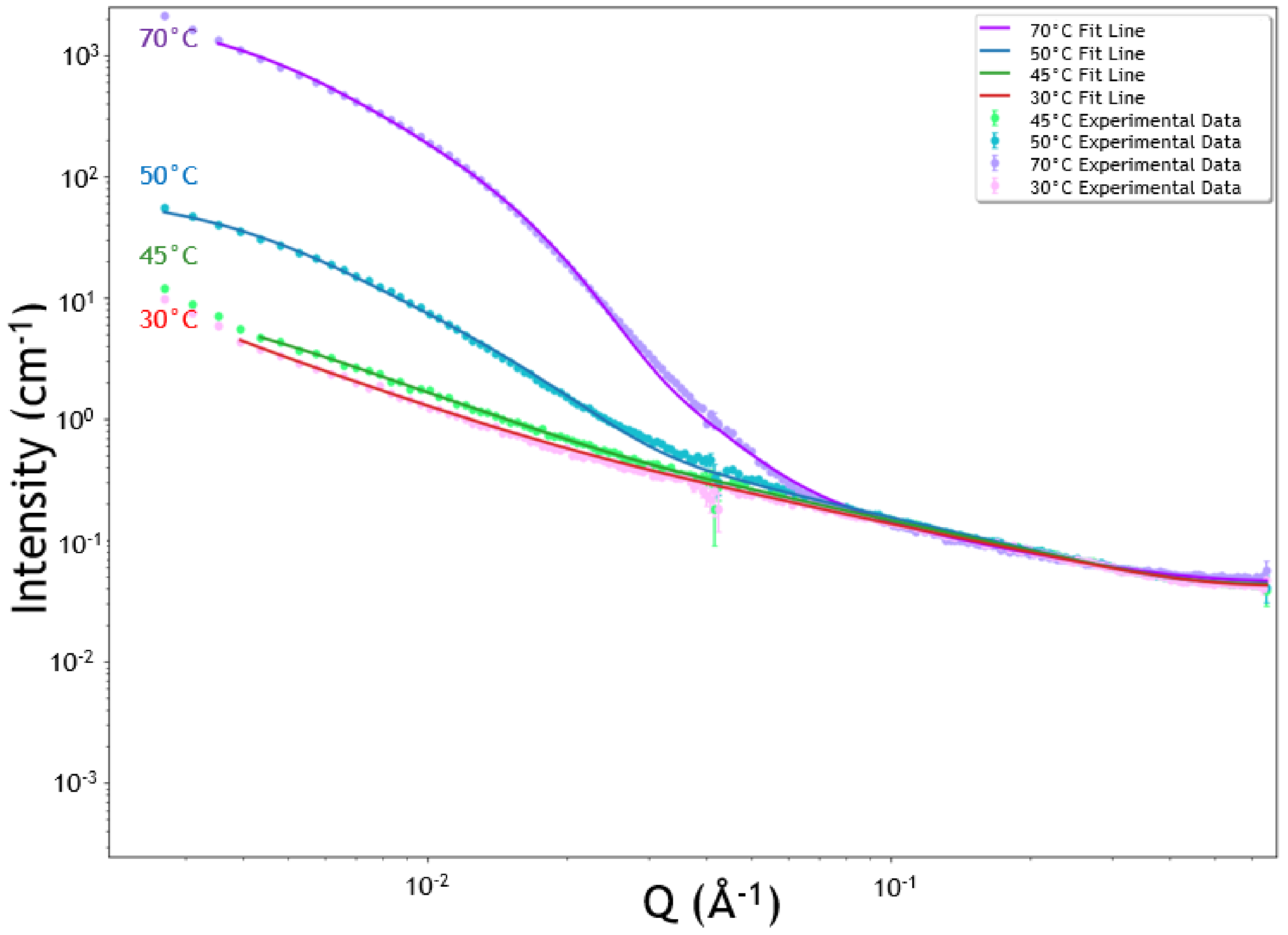
Thank You!

ANY QUESTIONS?

Gelation Temperature and Low-Shear Behavior	Predicting High-Shear Behavior	SANS Fitting and Nanostructure





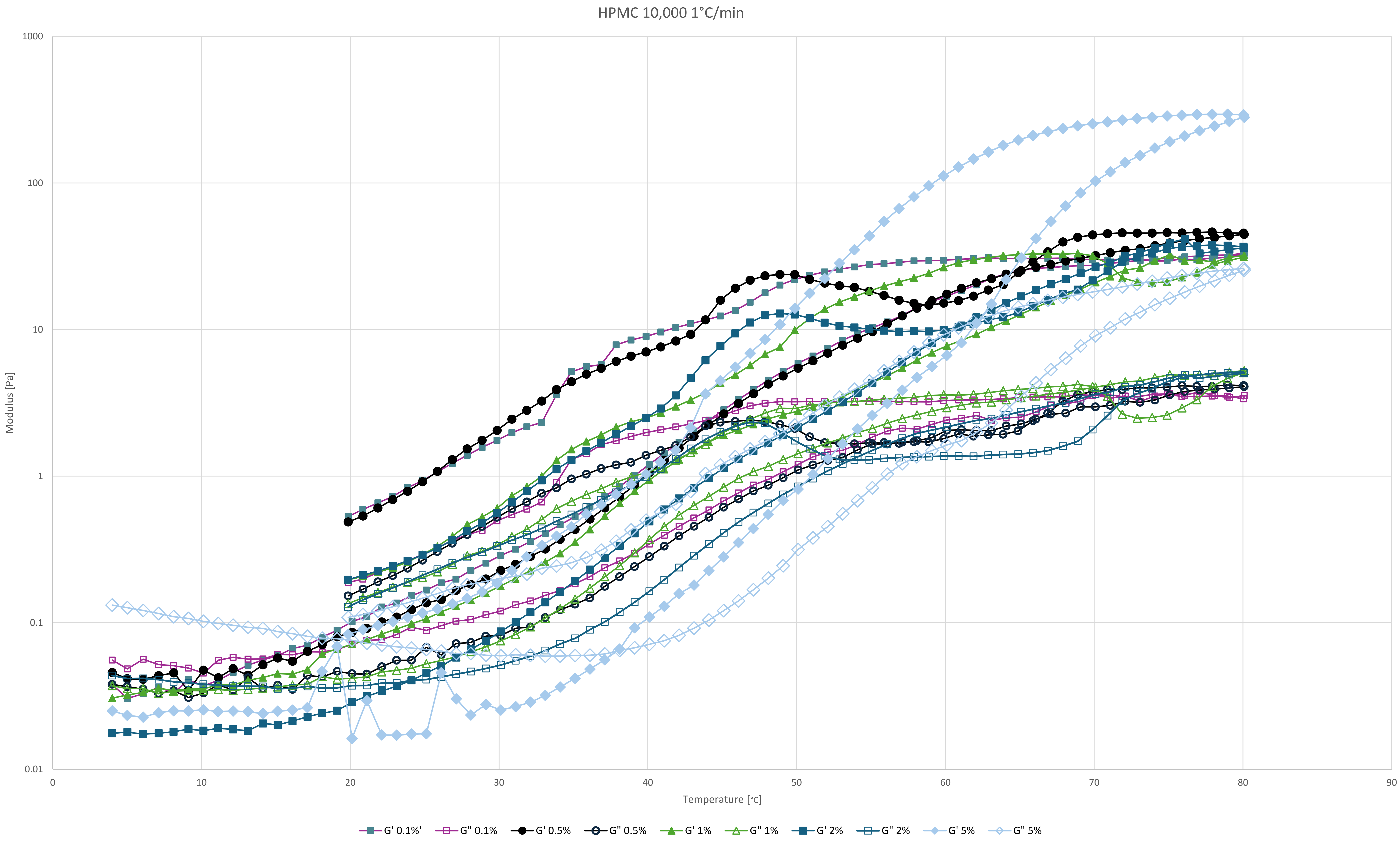


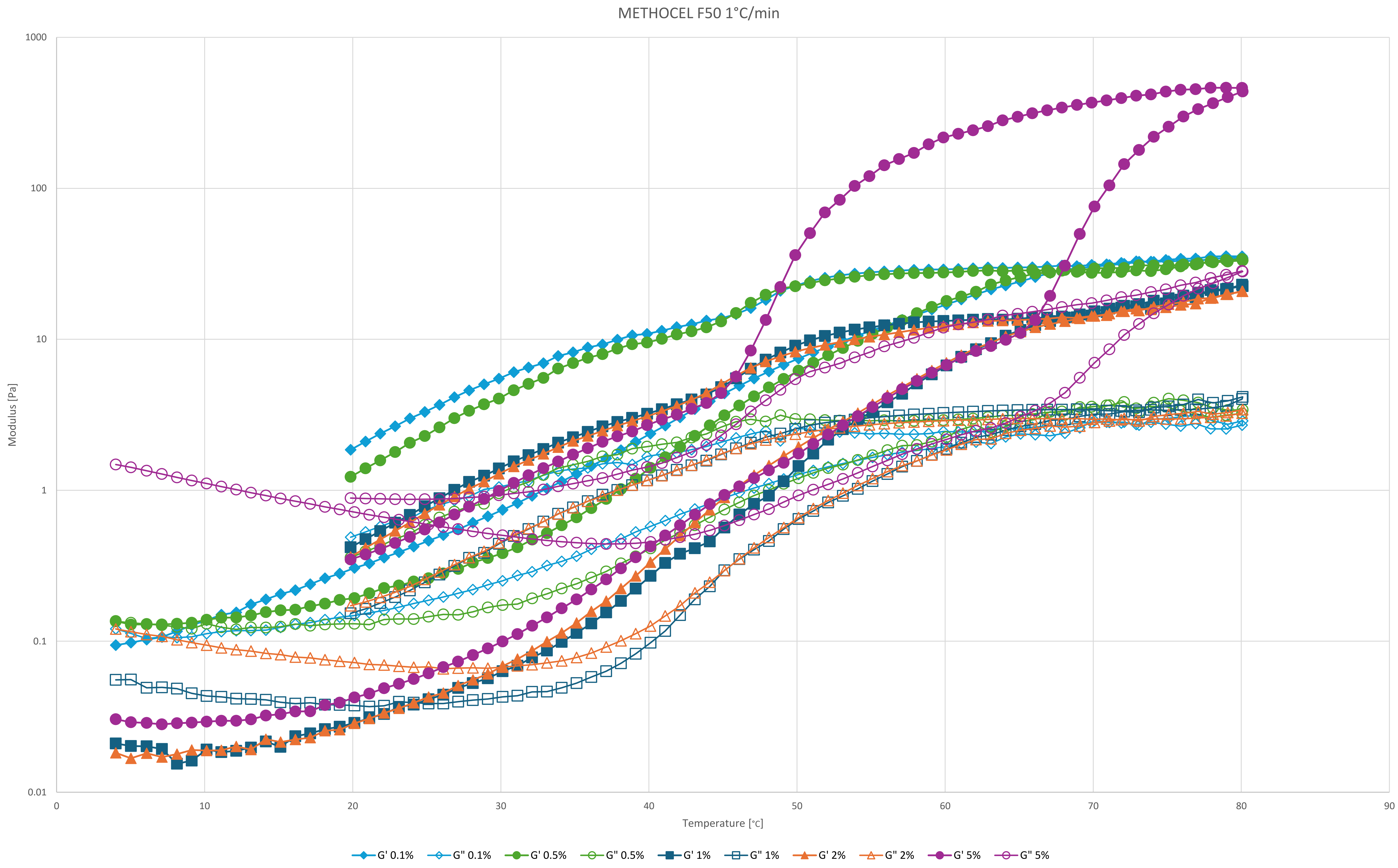
Backup Slides

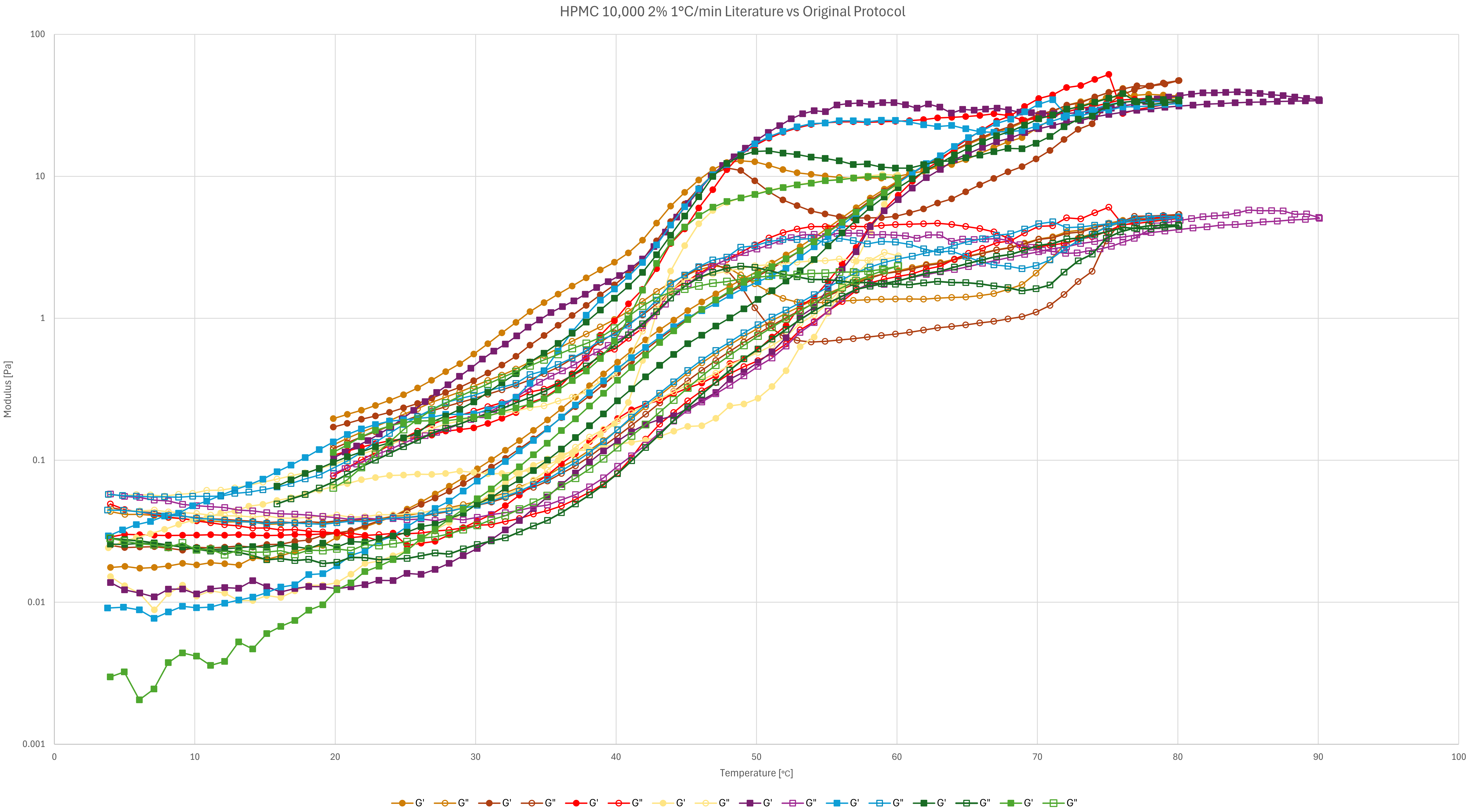
Zero-Shear Values

Temp	METHOCEL F50 0.1%	METHOCEL F50 0.5%	METHOCEL F50 1%	METHOCEL F50 2%	METHOCEL F50 5%
10	0.008647798	0.01207669	0.023750271	0.074341714	1.107095833
20	0.004514983	0.008244954	0.014924329	0.047647095	0.690322727
30	0.003253209	0.00498783	0.009753655	0.032852063	0.462120588
40	0.002531839	0.003763667	0.007194839	0.023095545	0.3476

Temp	HPMC Mn-10,000 0	HPMC Mn-10,000 0.!	HPMC Mn-10,000 1%	HPMC Mn-10,000 2%	HPMC Mn-10,000 5%
10	0.008144768	0.011954906	0.009844437	0.016367111	0.079828115
20	0.004587182	0.007133333	0.006096339	0.010536683	0.0514325
30	0.002973236	0.00501565	0.004590383	0.00729483	0.035666645
40	0.002015794	0.003155567	0.002823633		0.027156151

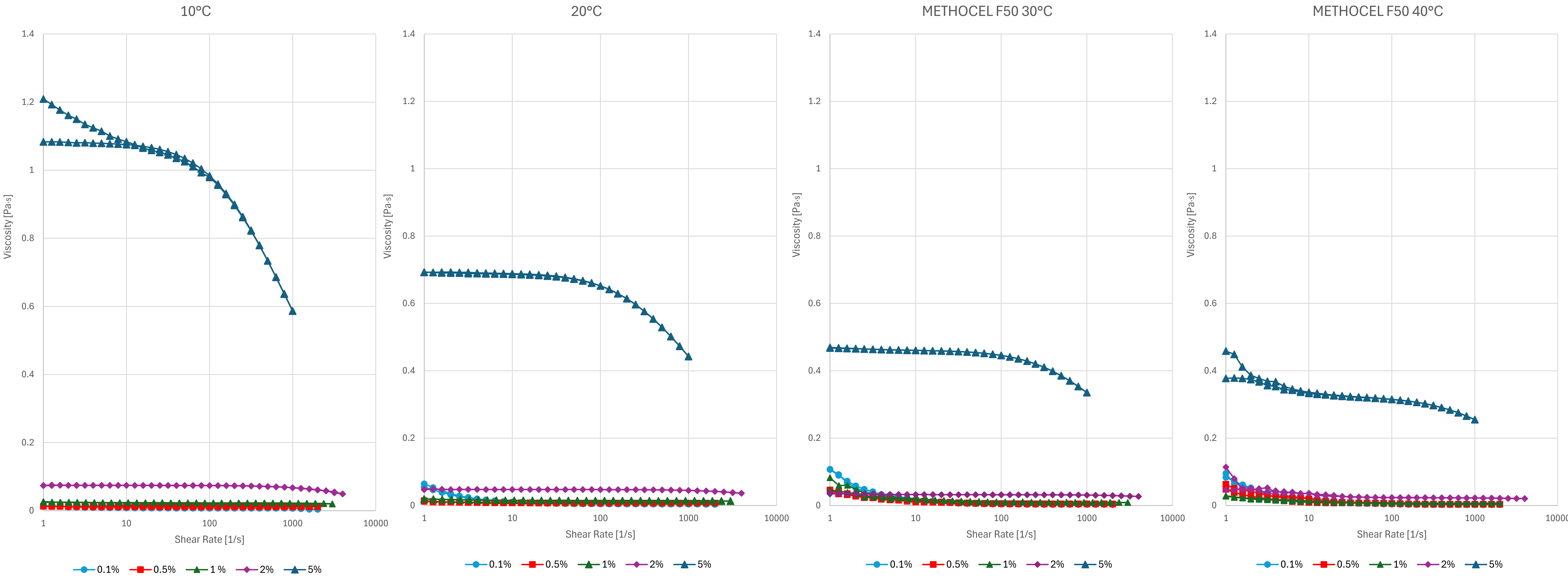

HPMC 10,000 1°C/min
Modulus [Pa]
1000
100
10
1
0.1
0.01
0
10
20
30
40
50
60
70
80
90
Temperature [℃]
G' 0.1%'
G" 0.1%
G' 0.5%
G" 0.5%
G' 1%
G" 1%
G' 2%
G" 2%
G' 5%
G" 5%

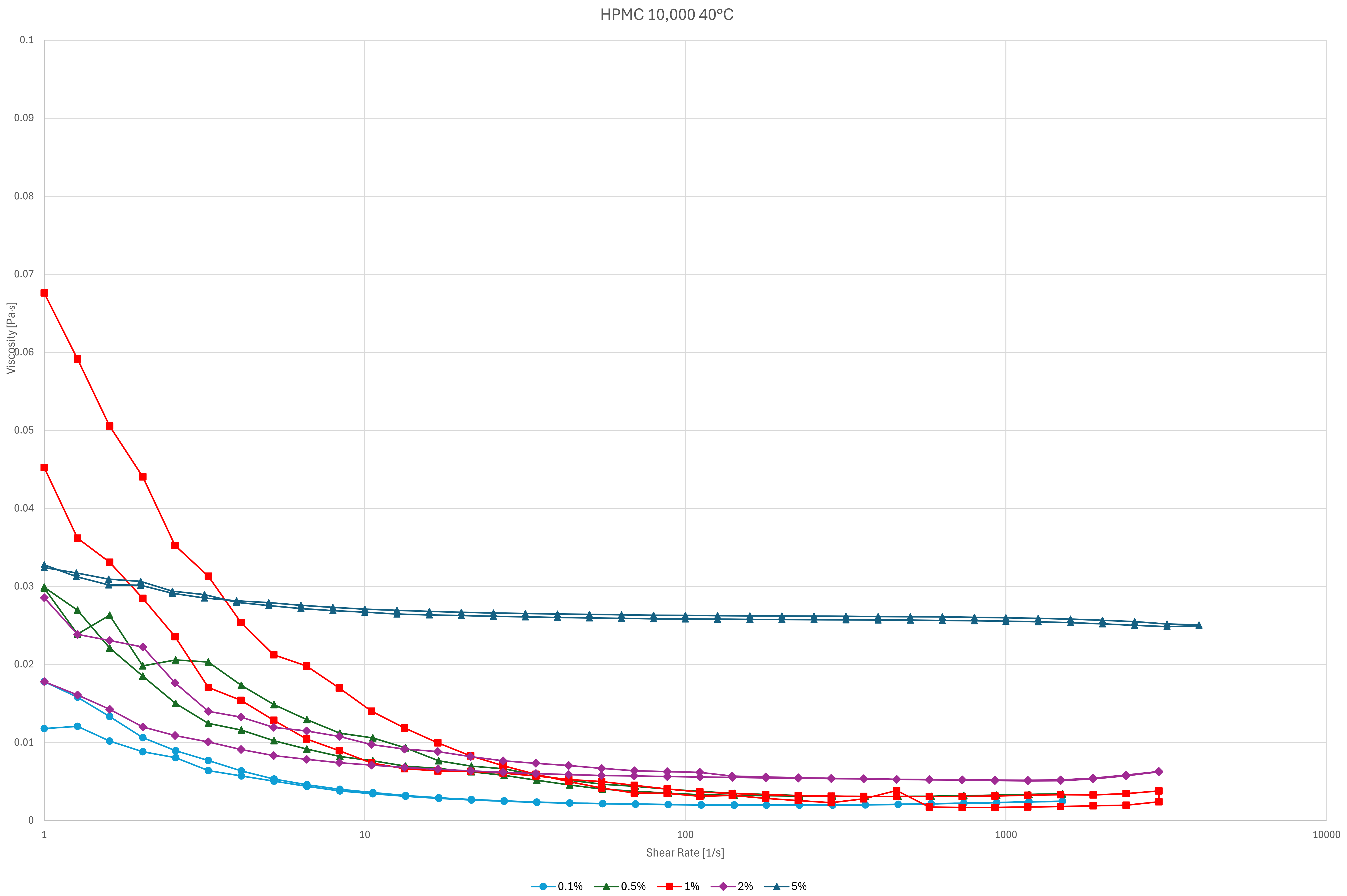

METHOCEL F50 1°C/min
Modulus [Pa]
1000
100
10
1
0.1
0.01
0
10
20
30
40
50
60
70
80
90
Temperature [°C]
G' 0.1%
G" 0.1%
G' 0.5%
G" 0.5%
G' 1%
G" 1%
G' 2%
G" 2%
G' 5%
G" 5%

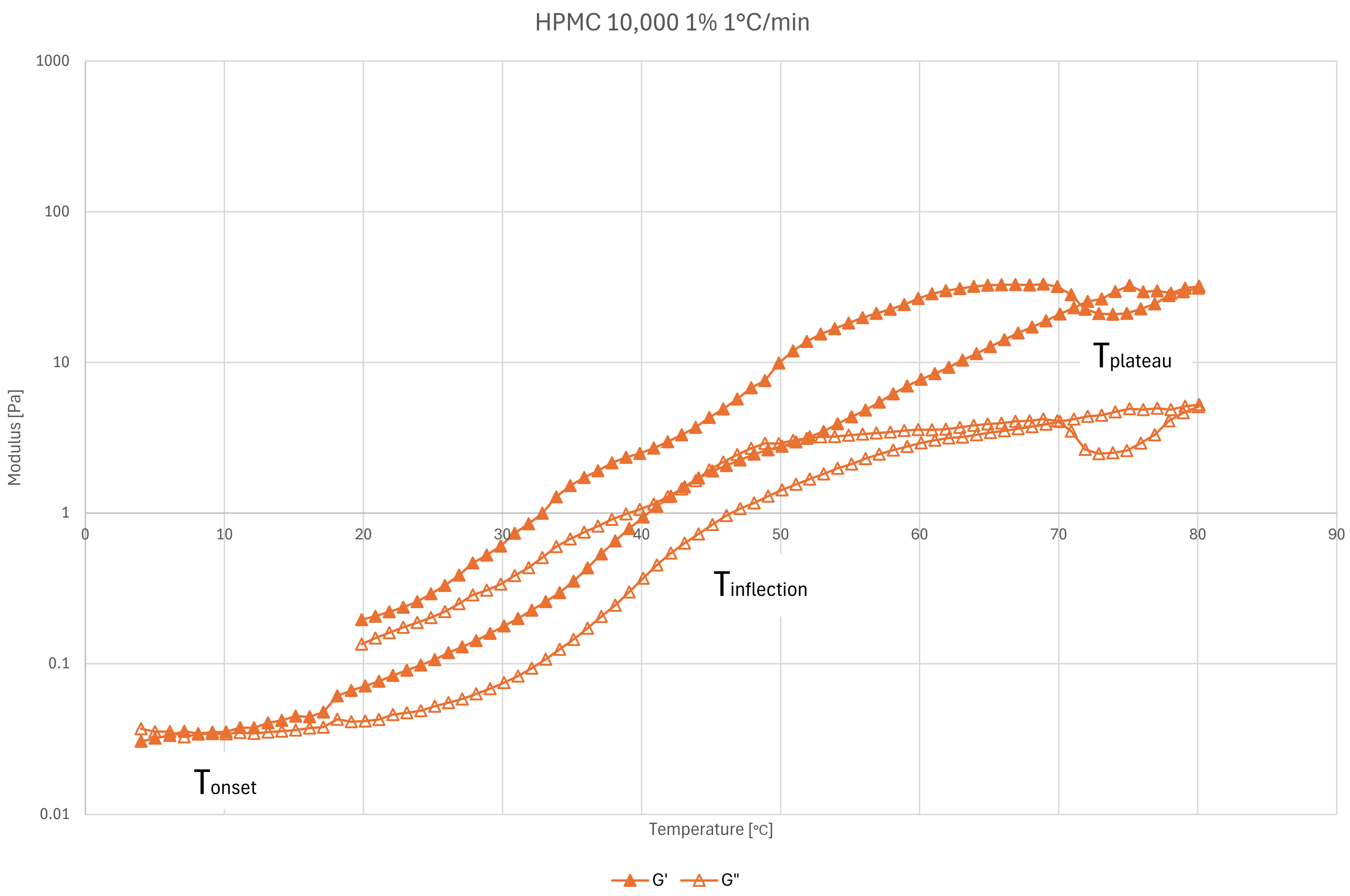


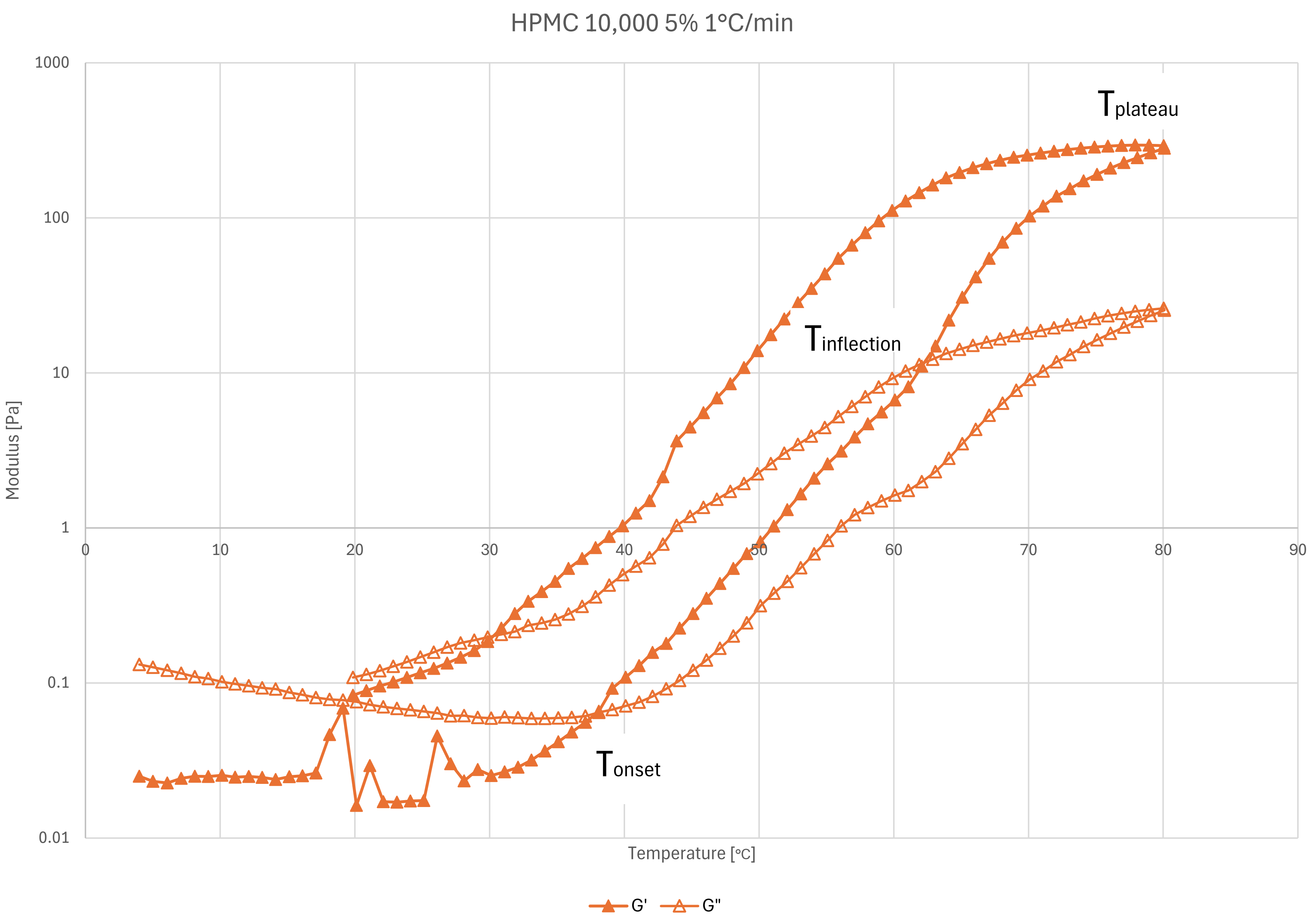
HPMC 10,000 2% 1°C/min Literature vs Original Protocol
Modulus [Pa]
100
10
1
0.1
0.01
0.001
0
10
20
30
40
50
60
70
80
90
100
Temperature [ºC]
G'
G"
G'
G"
G'
G"
G'
G"
G'
G"
G'
G"
G'
G"
G'
G"

METHOCEL F50 Steady-Shear Ramps




HPMC 10,000 40°C
Viscosity [Pa·s]
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
1
10
100
1000
10000
Shear Rate [1/s]
0.1%
0.5%
1%
2%
5%


HPMC 10,000 1% 1°C/min
Modulus [Pa]
1000
100
10
1
0.1
0.01
0
10
20
30
40
50
60
70
80
90
Temperature [ºC]
Tonset
Tinflection
Tplateau
G'
G"


HPMC 10,000 5% 1°C/min
Modulus [Pa]
1000
100
10
1
0.1
0.01
0
10
20
30
40
50
60
70
80
90
Temperature [ºC]
Tonset
Tinflection
Tplateau
G'
G"

Gelation Temperature Quantifications

Storage Modulus	Loss Modulus	Complex Modulus	Temperature	G' Derivative	G" Derivative
[Pa]	[Pa]	[Pa]	[°C]		
0.16512	0.4565	0.48544	34.11	0.000354333	0.000136833
0.18938	0.44937	0.48765	35.11	0.000404333	0.000118833
0.22037	0.44339	0.49513	36.11	0.0005165	9.96667E-05
0.25673	0.44099	0.51028	37.11	0.000606	4E-05
0.30371	0.44165	0.536	38.11	0.000783	1.1E-05
0.36001	0.44582	0.57304	39.11	0.000938333	6.95E-05
0.42513	0.45461	0.62242	40.11	0.001085333	0.0001465
0.50147	0.46972	0.6871	41.1	0.001272333	0.000251833
0.58634	0.48906	0.76353	42.1	0.0014145	0.000322333
0.68967	0.51201	0.85895	43.11	0.001722167	0.0003825
0.80865	0.54178	0.97336	44.11	0.001983	0.000496167
0.93039	0.58337	1.0982	45.1	0.002029	0.000693167
6.0087	2.0278	6.3416	59.1	0.011768333	0.002481667
6.7564	2.1728	7.0972	60.1	0.012461667	0.002416667
7.5526	2.3336	7.9049	61.09	0.01327	0.00268
8.3609	2.4738	8.7192	62.09	0.013471667	0.002336667
9.0282	2.5839	9.3907	63.09	0.011121667	0.001835
9.9115	2.7926	10.297	64.1	0.014721667	0.003478333
10.998	3.0757	11.42	65.09	0.018108333	0.004718333
13.407	3.3681	13.824	66.09	0.04015	0.004873333
19.396	3.7869	19.762	67.09	0.099816667	0.00698
30.717	4.4225	31.033	68.09	0.188683333	0.010593333
49.78	5.5588	50.09	69.09	0.317716667	0.018938333

Storage Modulus	Loss Modulus	Complex Modulus	Temperature	G' Derivative	G" Derivative
[Pa]	[Pa]	[Pa]	[°C]		
49.78	5.5588	50.09	69.09	0.317716667	0.018938333
75.792	6.9927	76.114	70.09	0.433533333	0.023898333
104.64	8.5881	104.99	71.09	0.4808	0.02659
144.56	10.682	144.96	72.09	0.665333333	0.034898333
179.33	12.641	179.77	73.09	0.5795	0.03265
219.62	14.872	220.12	74.09	0.6715	0.037183333
255.94	16.987	256.5	75.09	0.605333333	0.03525
299.16	19.404	299.79	76.09	0.720333333	0.040283333
334.65	21.627	335.35	77.09	0.5915	0.03705
365.89	23.481	366.64	78.09	0.520666667	0.0309
401.42	25.684	402.24	79.09	0.592166667	0.036716667
438.19	28.079	439.09	80.09	0.612833333	0.039916667
462.44	28.35	463.31	80.05	0.404166667	0.004516667
463.7	26.735	464.47	78.97	0.021	0.026916667
463.65	25.443	464.35	77.93	0.000833333	0.021533333
453.56	23.731	454.18	76.91	0.168166667	0.028533333
449.67	22.811	450.24	75.9	0.064833333	0.015333333
436.98	21.429	437.51	74.9	0.2115	0.023033333
418.65	20.552	419.15	73.9	0.3055	0.014616667
410.53	19.597	411	72.9	0.135333333	0.015916667
396.19	18.989	396.65	71.9	0.239	0.010133333

Model Equations

Cross model

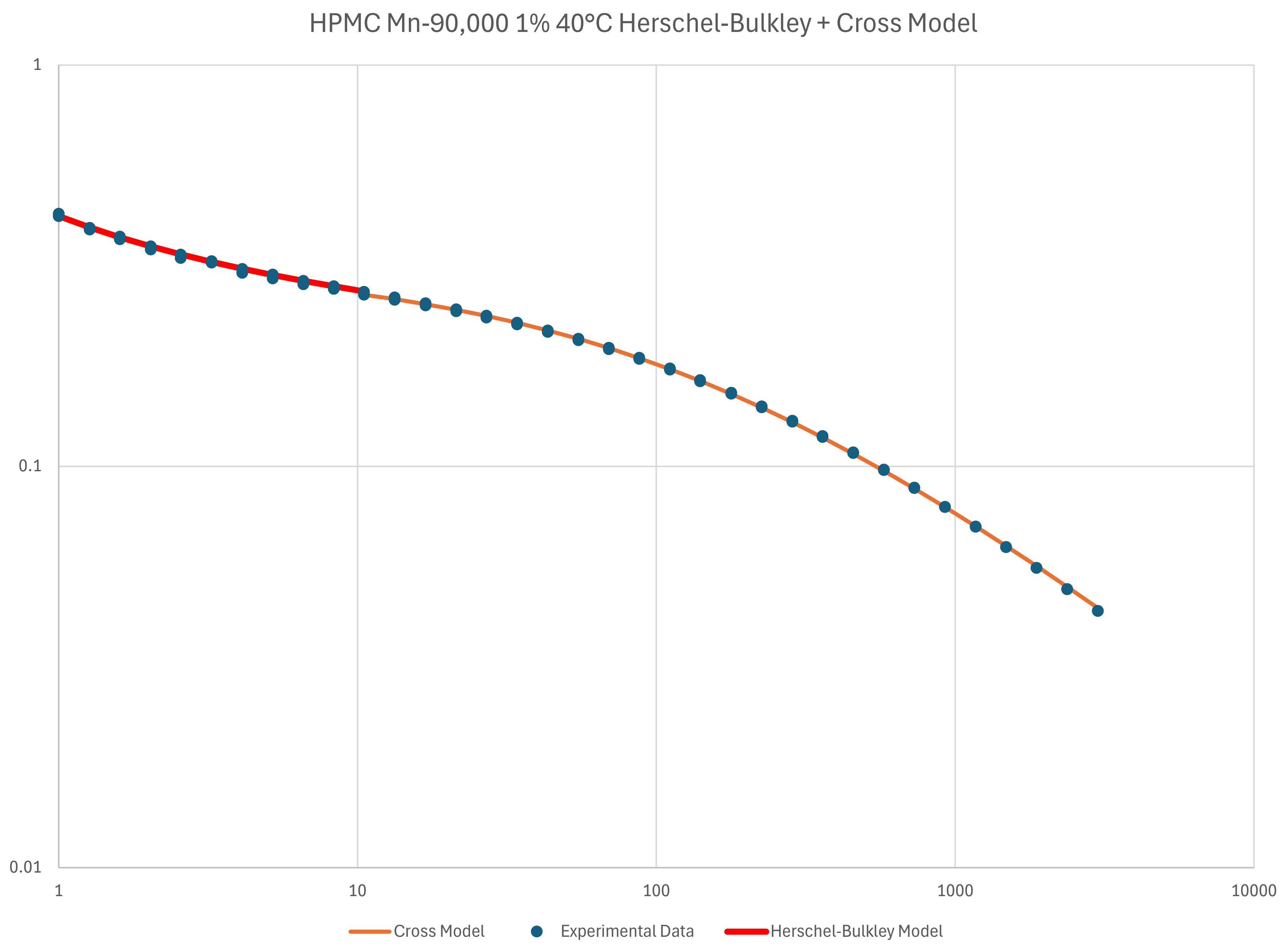
$$\eta = \eta_{\mathrm{inf}} + \frac{\eta_0 - \eta_{\mathrm{inf}}}{1 + (\alpha.\dot{\gamma})^n}$$

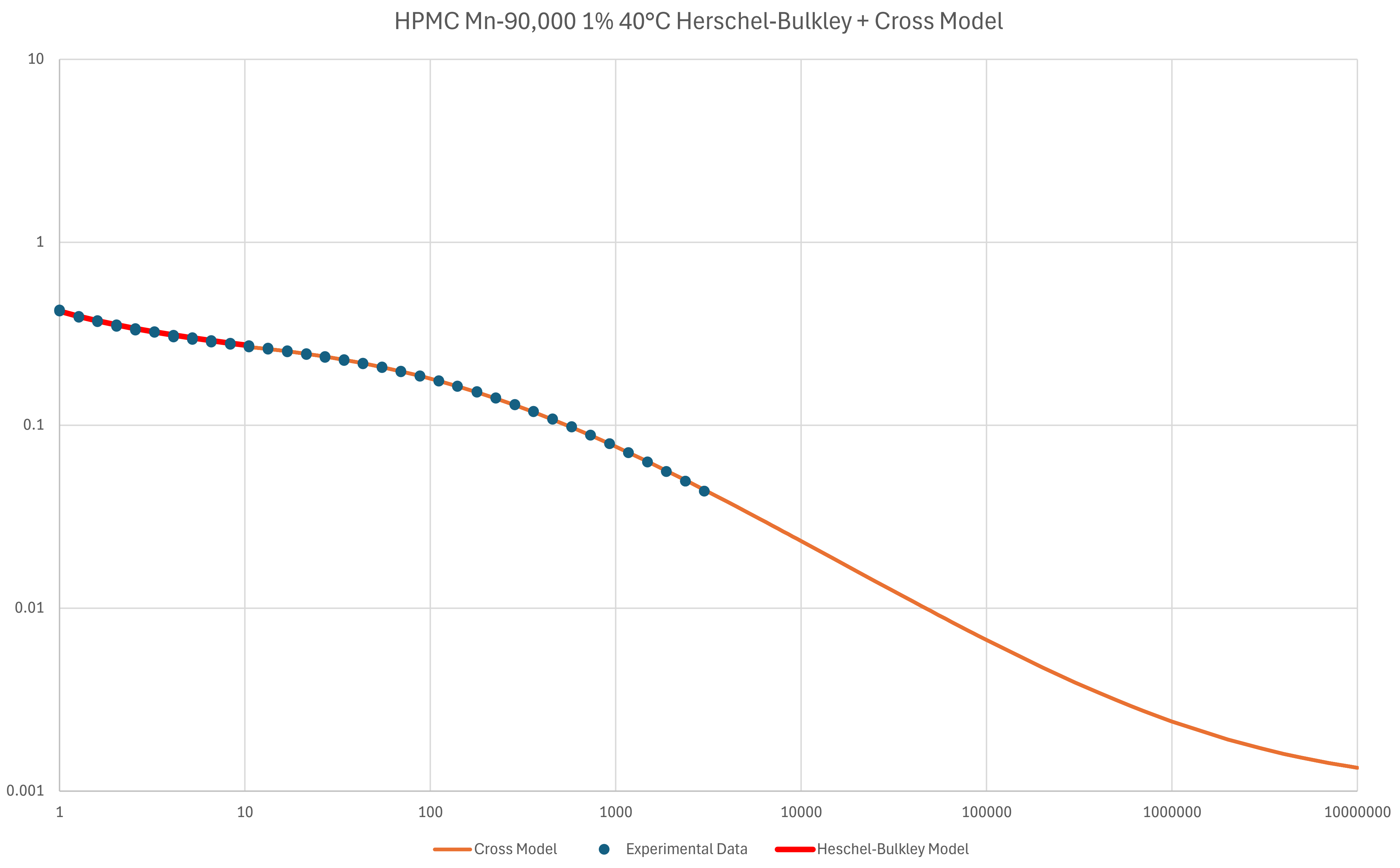
Herschel-Bulkley & Power Law

$$\tau = \tau_0 + K\dot{\gamma}^n$$

$$\eta = \frac{\tau_0 + K\dot{\gamma}^n}{\dot{\gamma}}$$

Herschel-Bulkley Model





Model Parameters

10°C

eta0	1.32	Pa-s
etainf	0.01	Pa-s
n	0.674577	slope
1/gamma_	0.030109	s
sum error	0.008163	

20°C

eta0	0.75	Pa-s
etainf	0.001	Pa-s
n	0.631343	slope
1/gamma_	0.015586	s
sum error	0.001051	

30°C

eta0	0.47	Pa-s
etainf	0.001	Pa-s
n	0.626374	slope
1/gamma_	0.009519	s
sum error	0.000174	

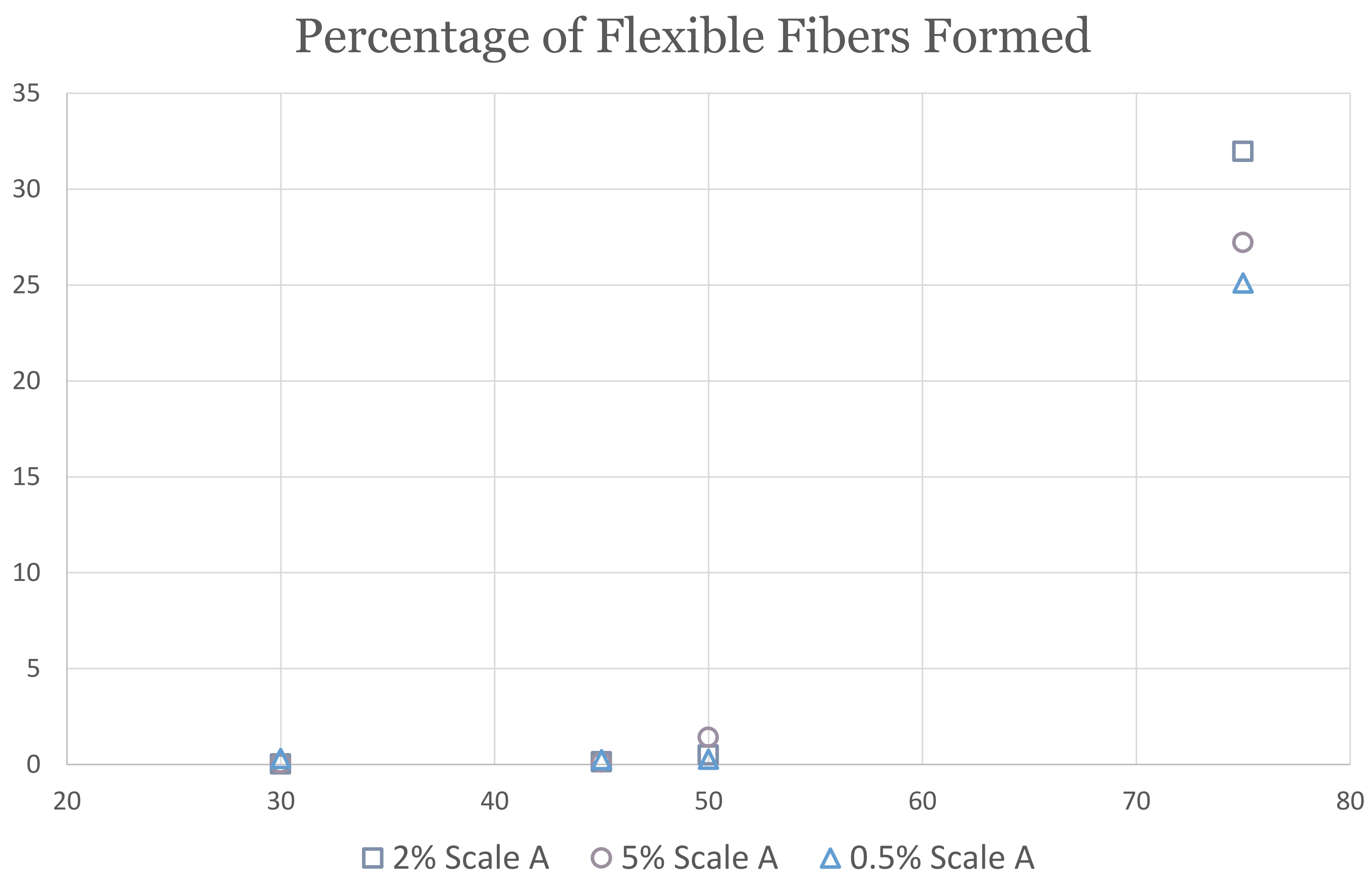
40°C

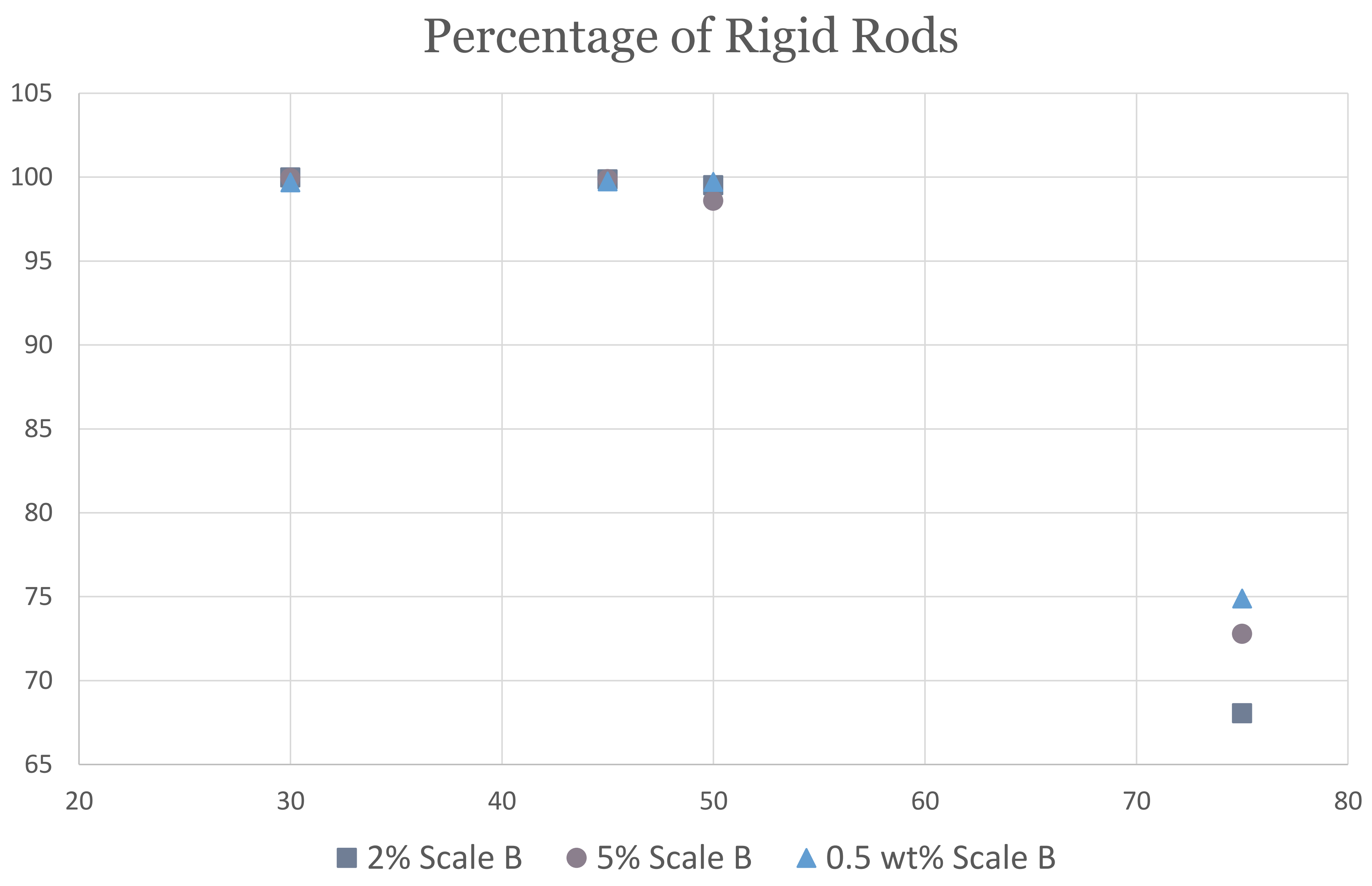
eta0	0.32	Pa-s
etainf	0.001	Pa-s
n	0.615155	slope
1/gamma_	0.006732	s
sum error	6.68E-05	

Yield Stress	0.08876678	
n	0.903606462	slope
K	0.331742985	
sum error	0.005738463	

SANS Parameters

Temp (°C)	Flexible Cylinder Scale	Flexible Cylinder Radius (Å)	Rigid Rod Scale	Rigid Rod Radius (Å)	Flexible Cylinder (%)	Rigid Rod (%)
30	0.00021432	114.49	0.38304	4.2016	0.055921092	99.94407891
45	0.00046356	84.543	0.36415	4.5044	0.127137345	99.87286265
50	0.0048335	87.989	0.33848	4.8748	1.407896864	98.59210314
75	0.12374	110.05	0.33088	4.0953	27.21833619	72.78166381


Percentage of Flexible Fibers Formed
35
30
25
20
15
10
5
0
20
30
40
50
60
70
80
2% Scale A
5% Scale A
0.5% Scale A


Percentage of Rigid Rods
105
100
95
90
85
80
75
70
65
20
30
40
50
60
70
80
2% Scale B
5% Scale B
0.5 wt% Scale B