“Rheological Behavior of Concentrated Suspensions as affected by the Degree of Mixedness of their Ingredients”

Joint Ordnance Commanders Group (JOCG)
Continuous Mixer & Extruder Users Group (CMEUG)
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Stevens Institute of Technology

HfMI’s structural analysis tools for the degree of mixedness of the ingredients of complex formulations

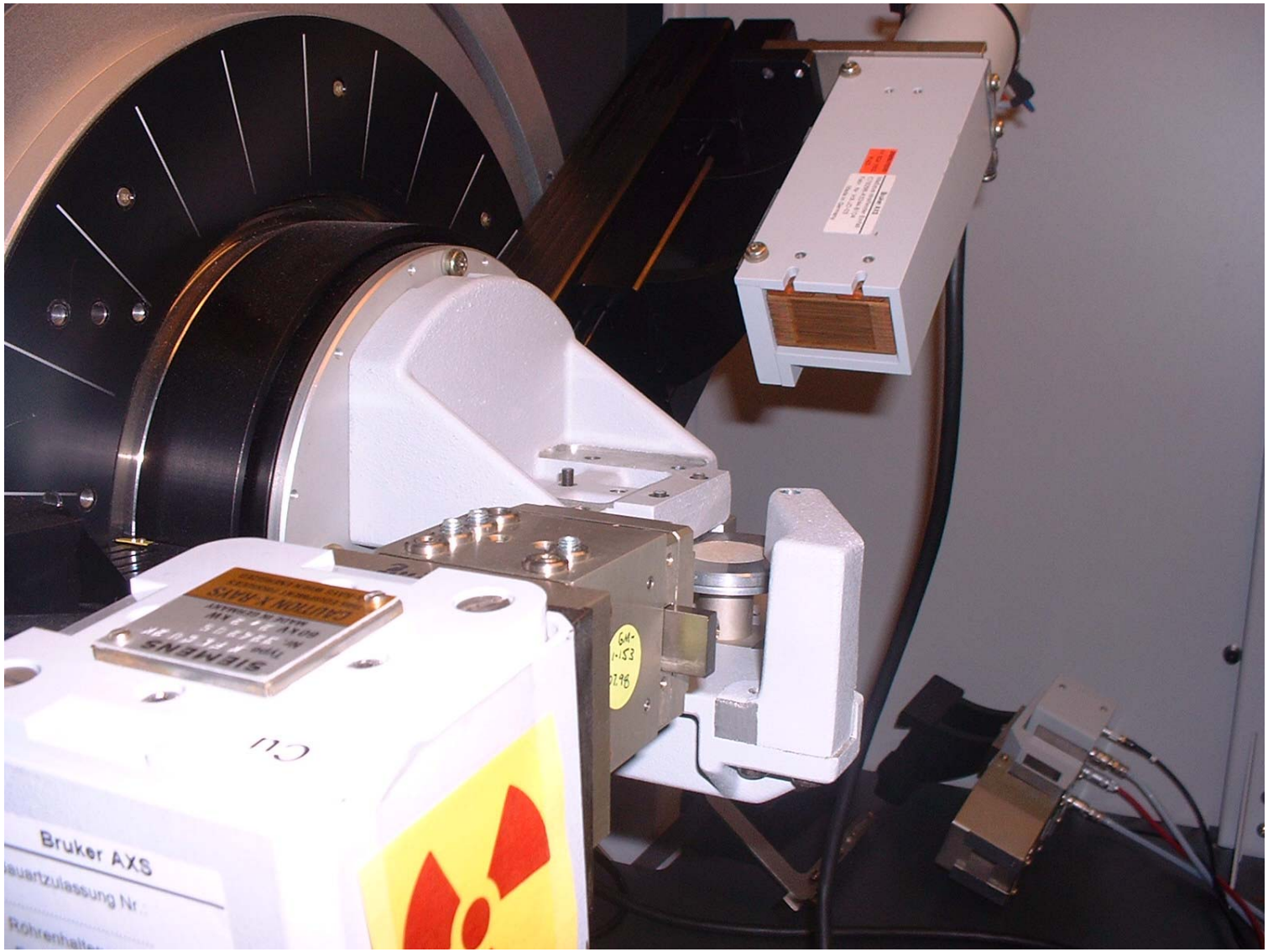
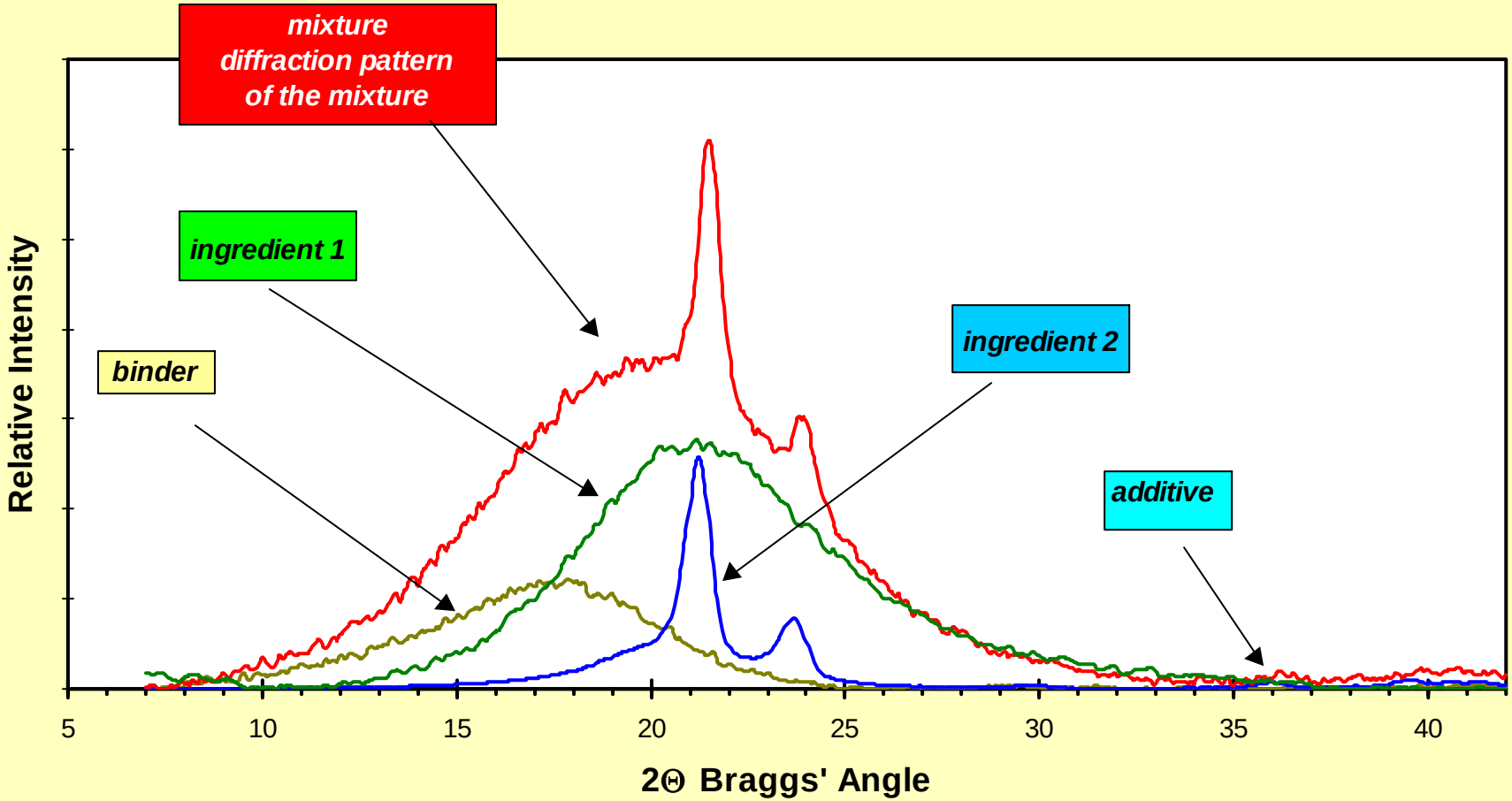
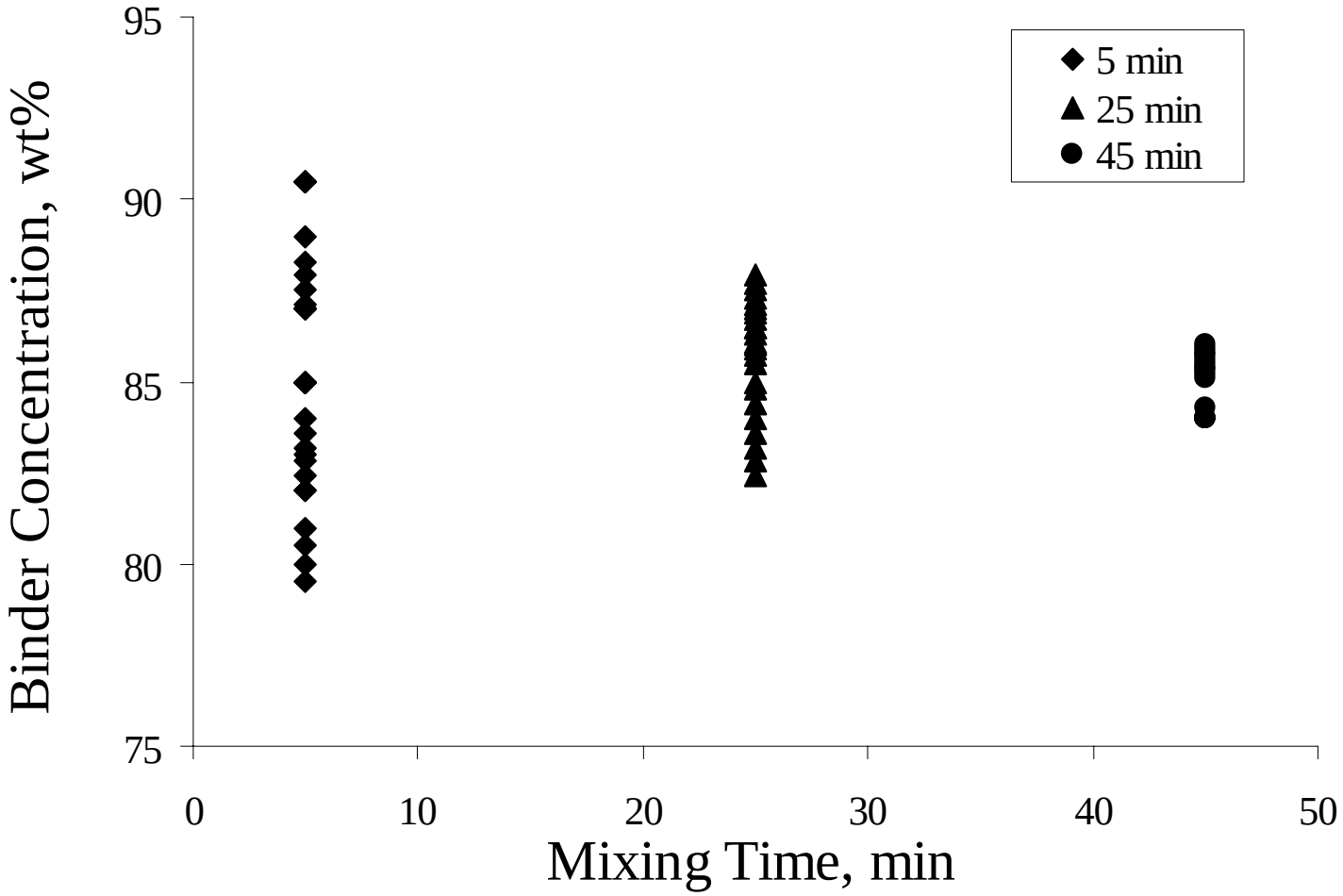

SIEMENS
Cu
Bruker AXS

Fig. 2 X-RAY DIFFRACTION PATTERN OF A MIXTURE AND ITS DECONVOLUTION TO ITS COMPONENTS




95
90
85
80
75
Binder Concentration, wt%
0
10
20
30
40
50
Mixing Time, min
5 min
25 min
45 min

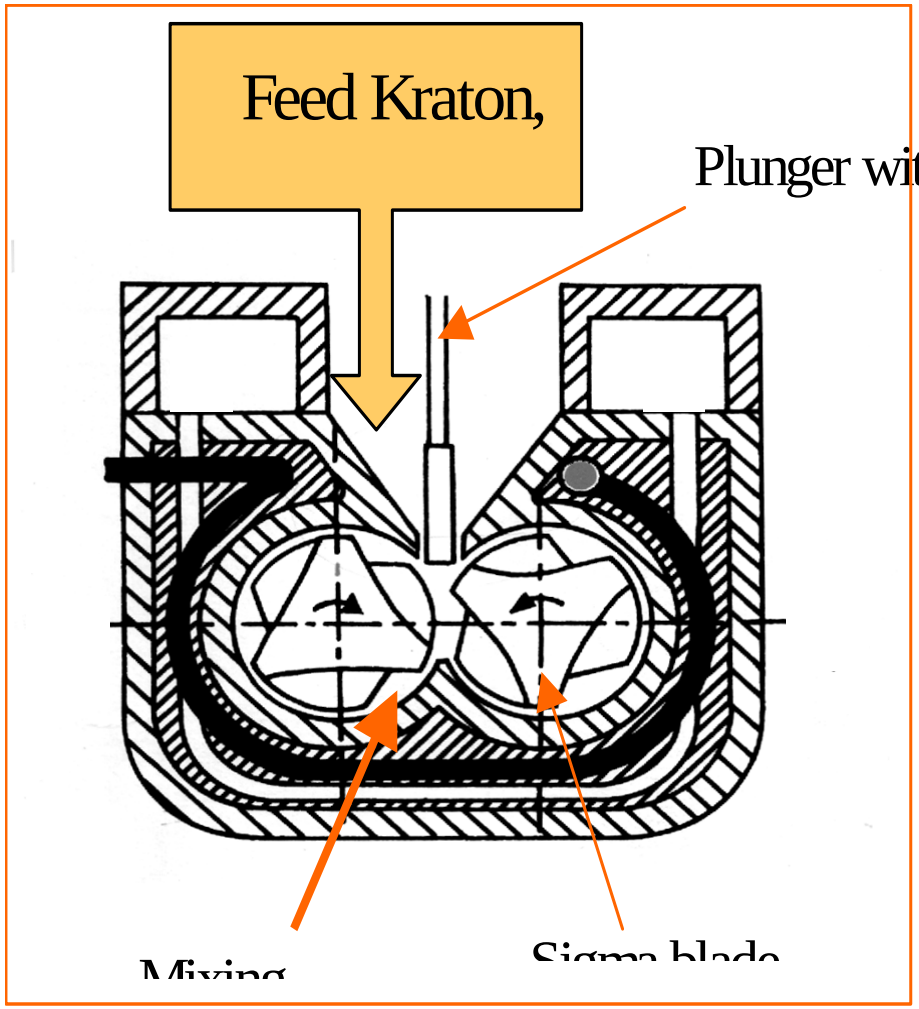
$$s^2 = \frac{1}{(N-1)} \sum_{i=1}^{N} \left(c_i - \bar{c}\right)^2$$

S is the standard deviation, C_i is the concentration,
$\bar{C}$ is the average, N is the number of specimens

$$s_0^2 = \bar{c}\left(1 - \bar{c}\right)$$

Variance for the completely segregated sample

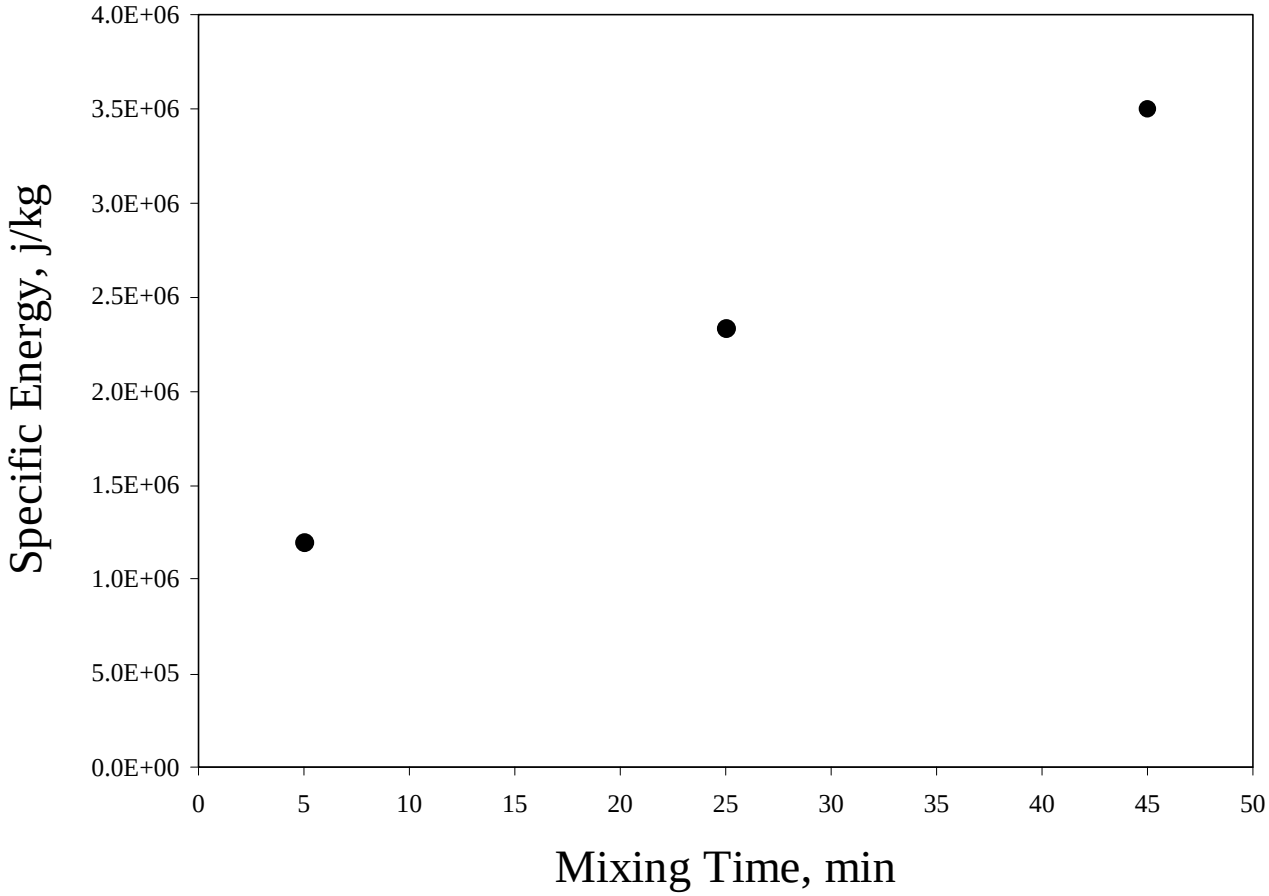
Mixing Index, MI = $\mathbf{1 - \boldsymbol{s/s_o}}$

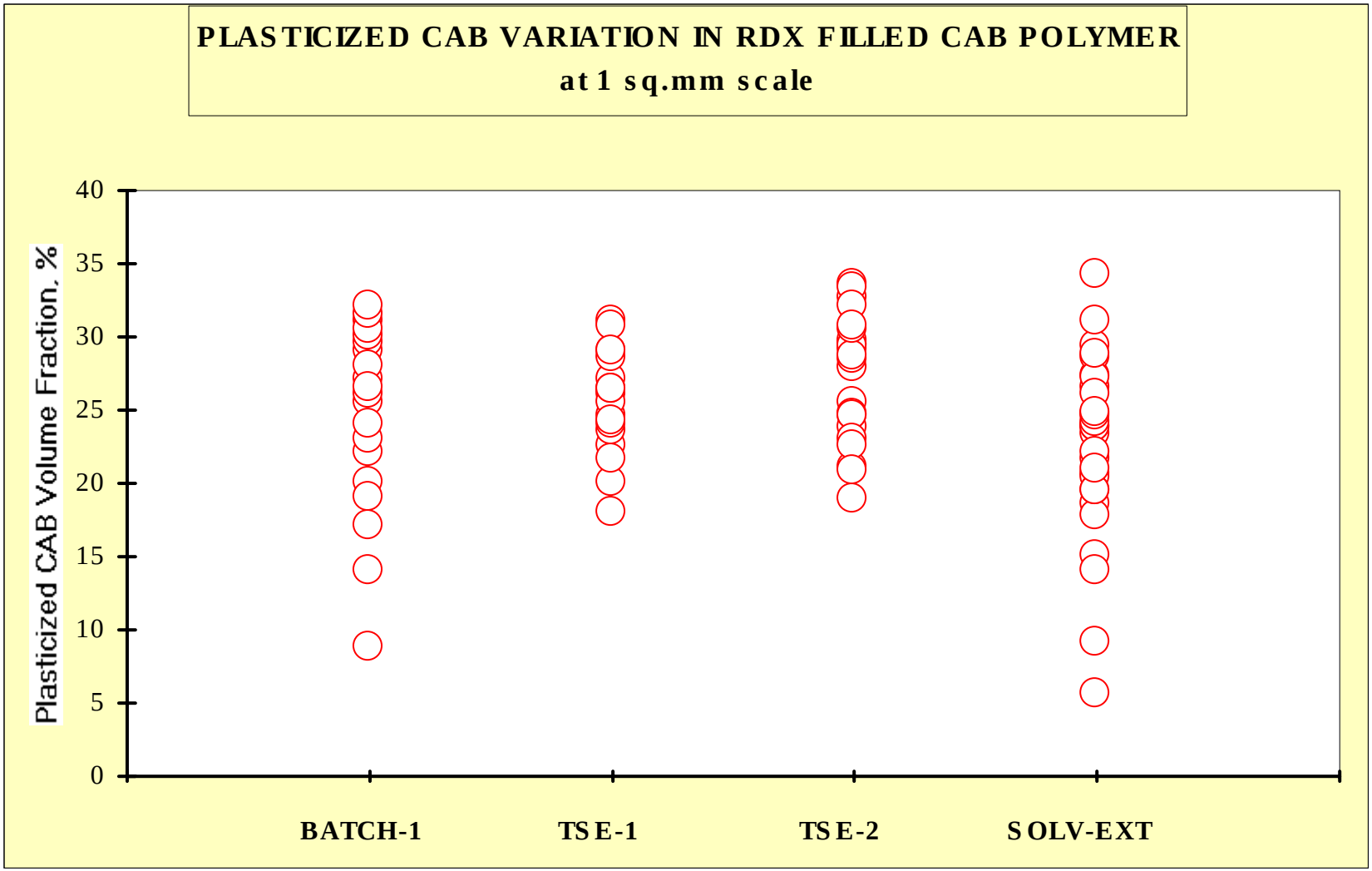

Feed Kraton,
Plunger with
Mixing
Sigma blade

Specific energy input, E_s is equal to:

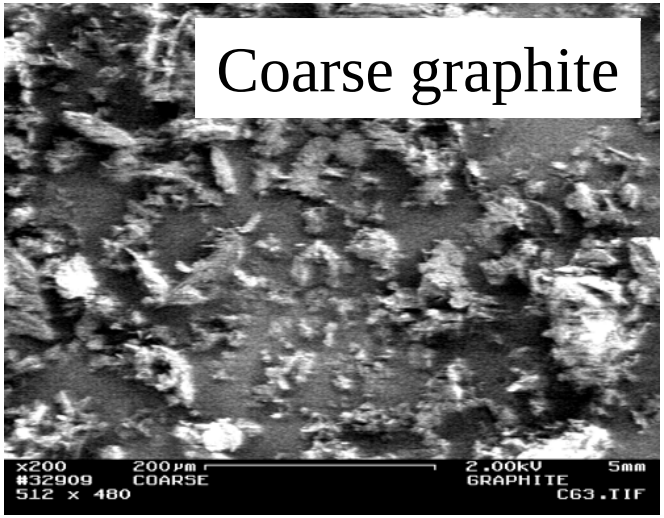
$$(2\pi\omega / Mt)\int \tau dt$$

ω is the rotational speed, M_t is the total amount of material in the mixer, τ is the torque varying as a function of time

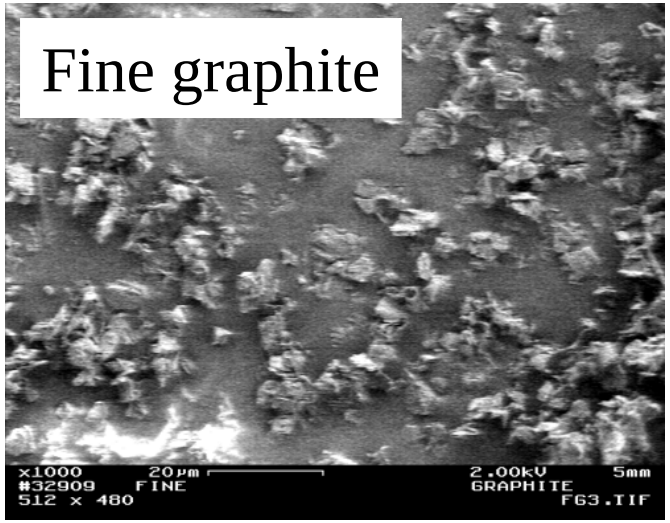

4.0E+06
3.5E+06
3.0E+06
2.5E+06
2.0E+06
1.5E+06
1.0E+06
5.0E+05
0.0E+00
Specific Energy, j/kg
0
5
10
15
20
25
30
35
40
45
50
Mixing Time, min

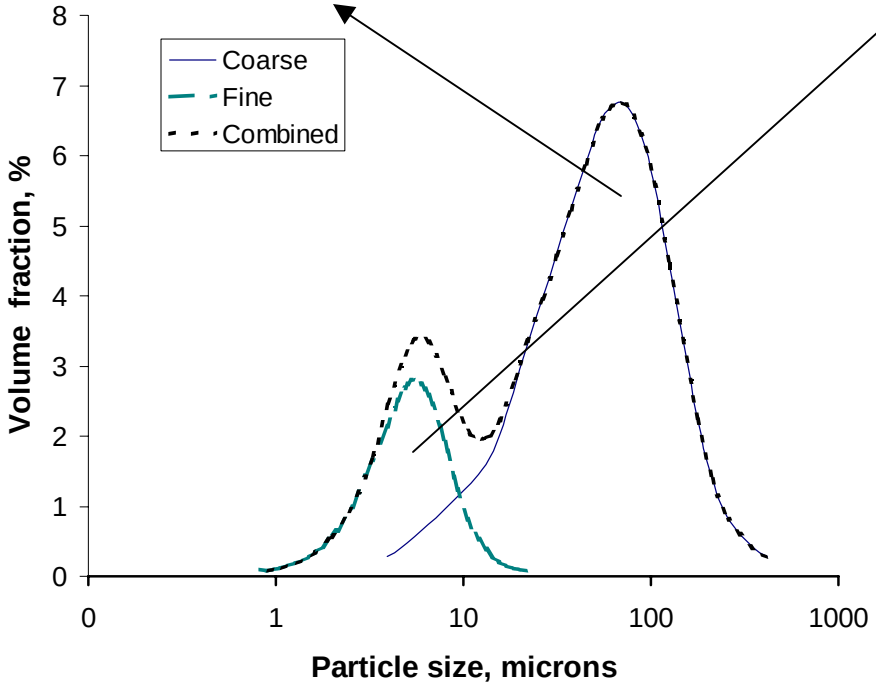

PLASTICIZED CAB VARIATION IN RDX FILLED CAB POLYMER
at 1 sq.mm scale
Plasticized CAB Volume Fraction, %
40
35
30
25
20
15
10
5
0
BATCH-1
TSE-1
TSE-2
SOLV-EXT

a)

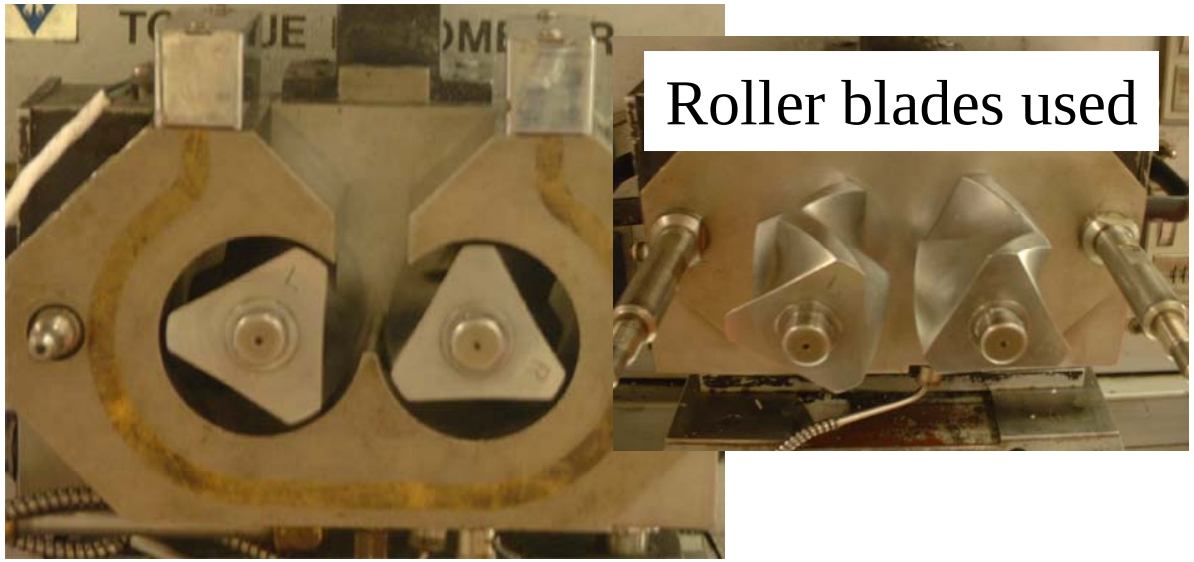


b)

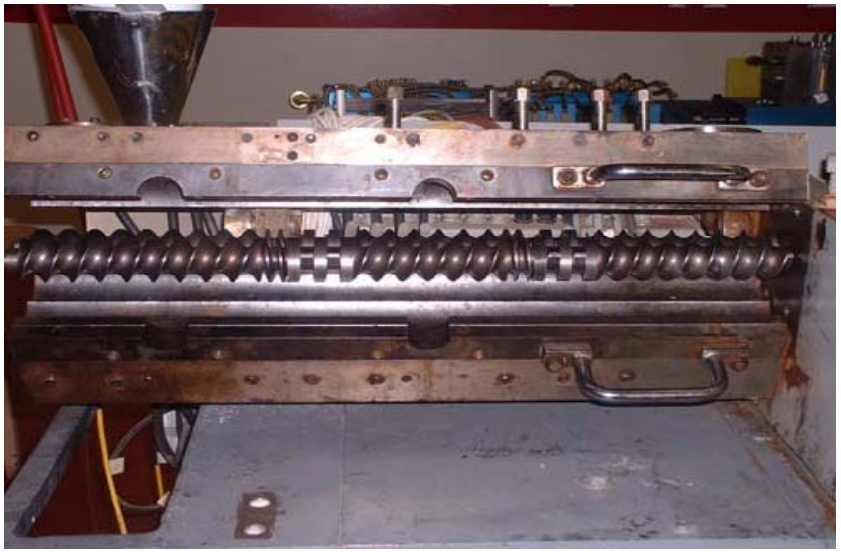




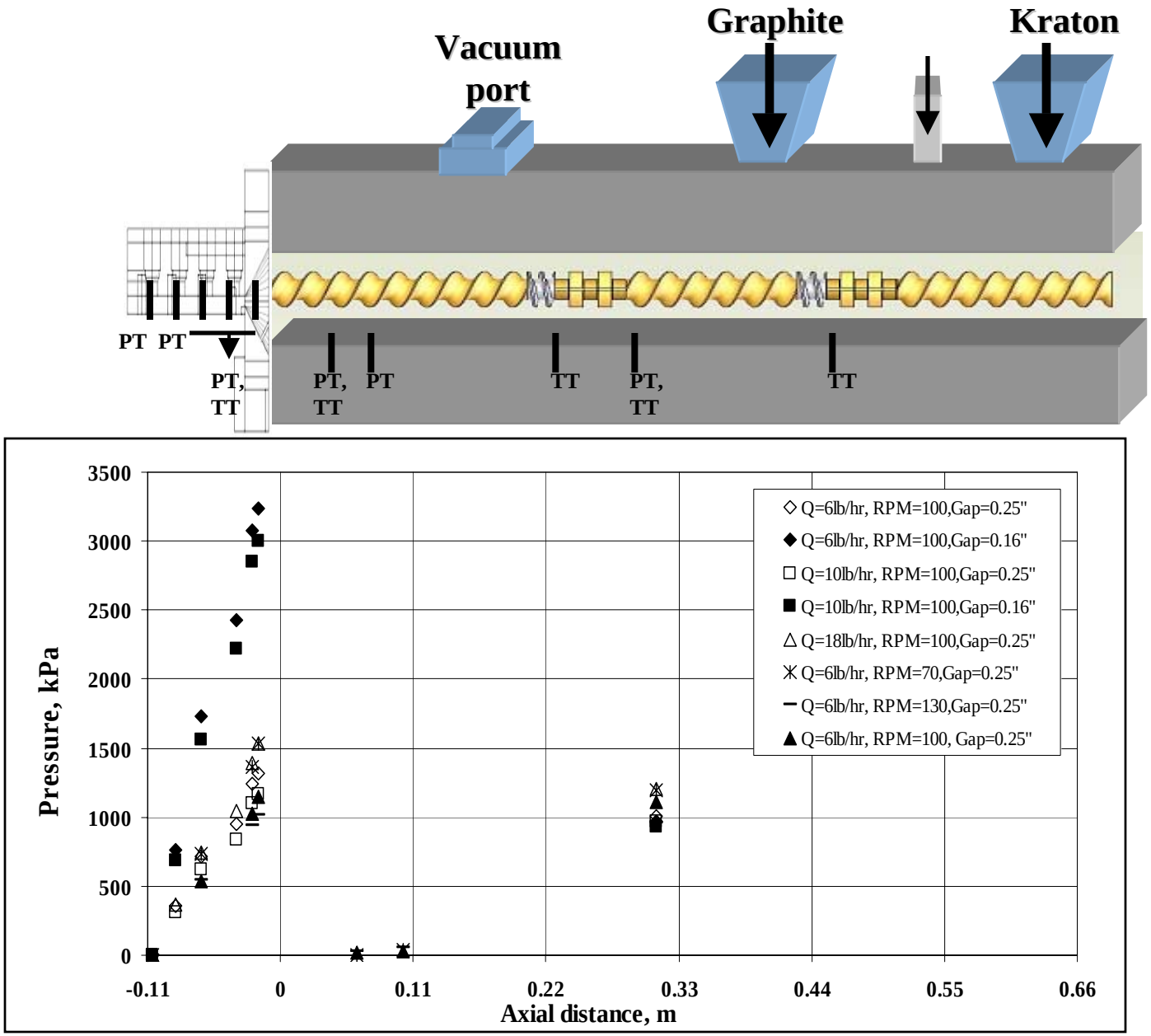
C) **Particle size distribution of coarse graphite and fine graphite and their mixture**



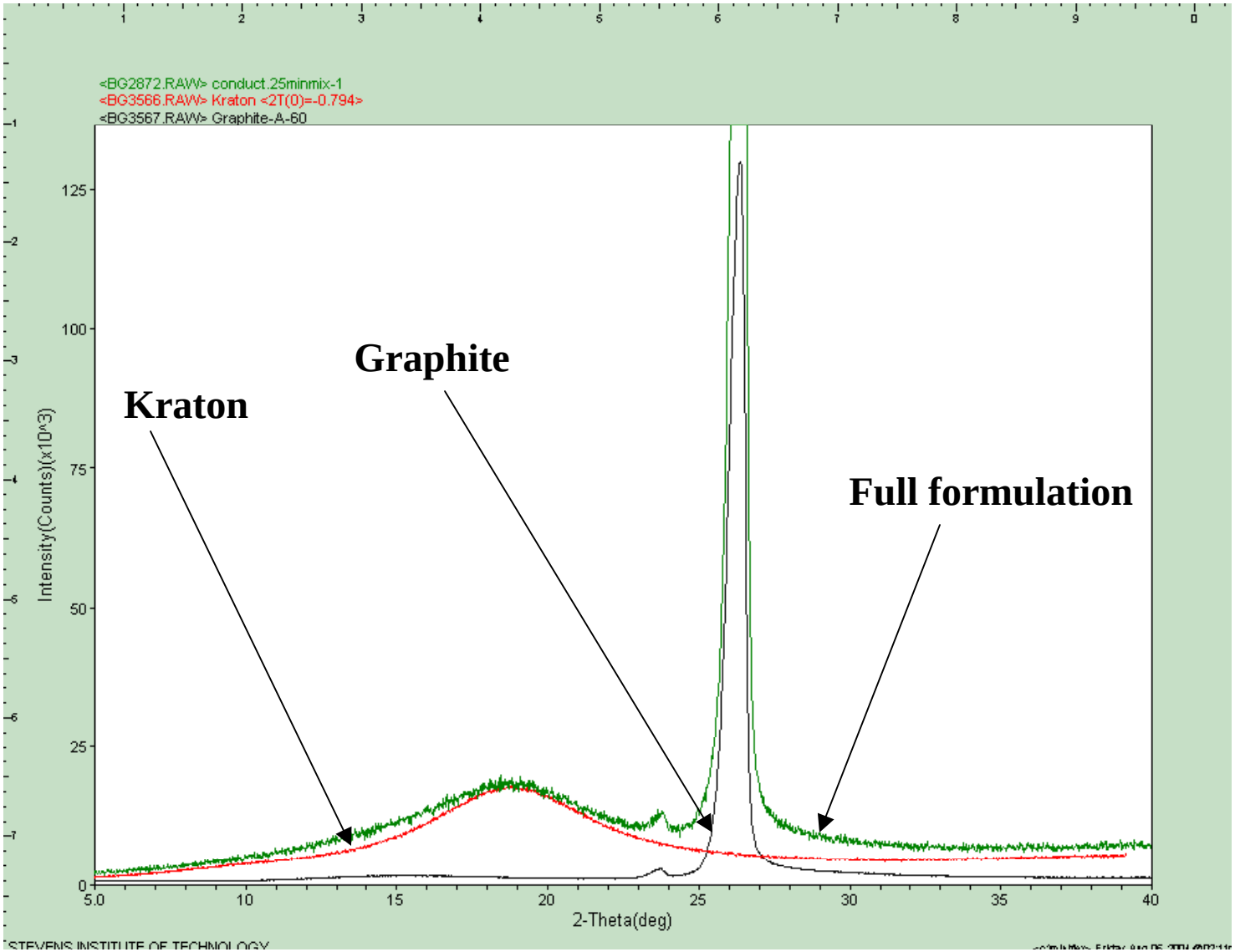
a) Haake Torque Rheometer and Batch Mixer



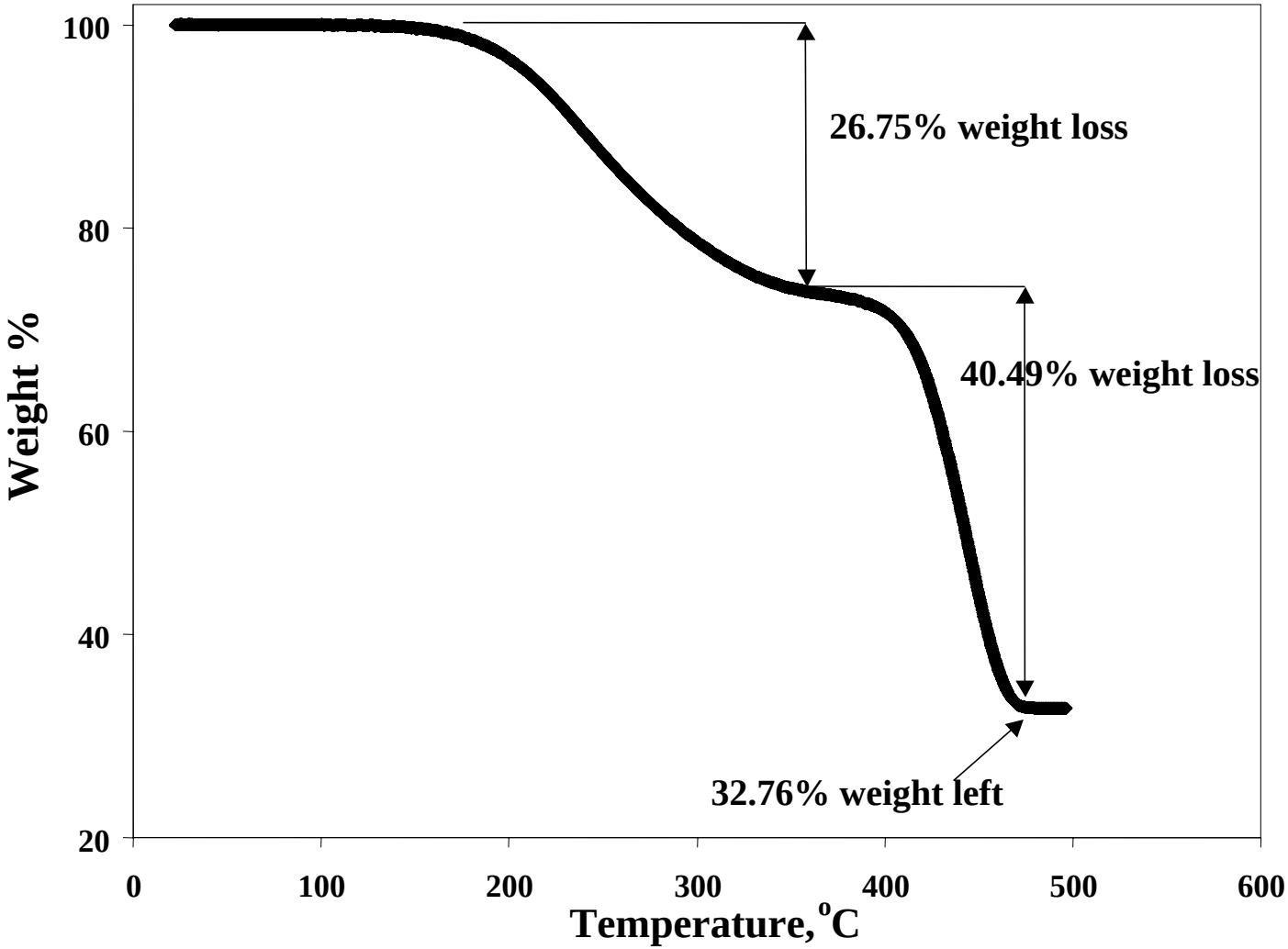
b) Fully intermeshing, co-rotating twin-screw extruder



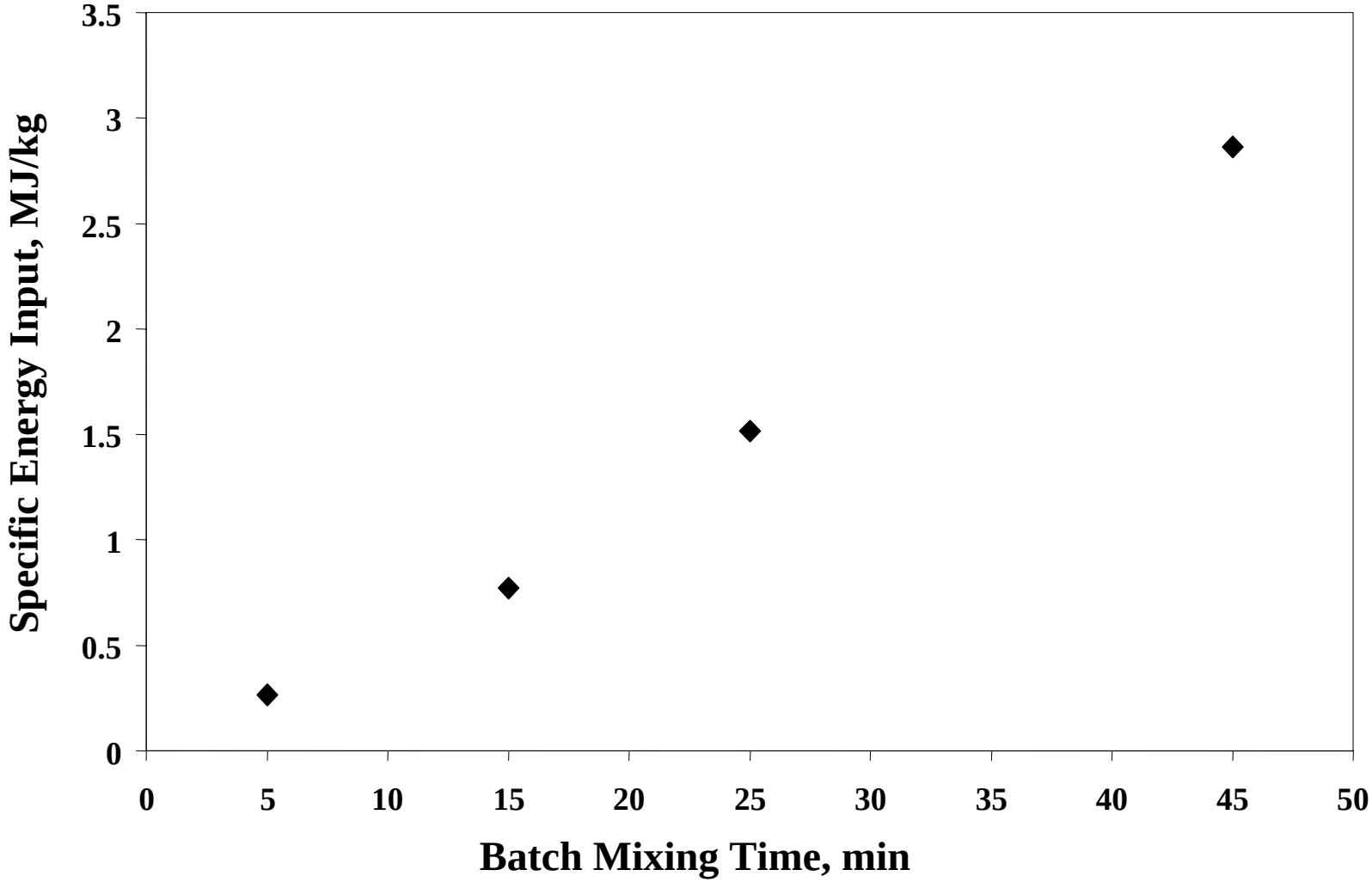
Screw configuration and the typical pressure readings from co-rotating twin screw extrusion experiments

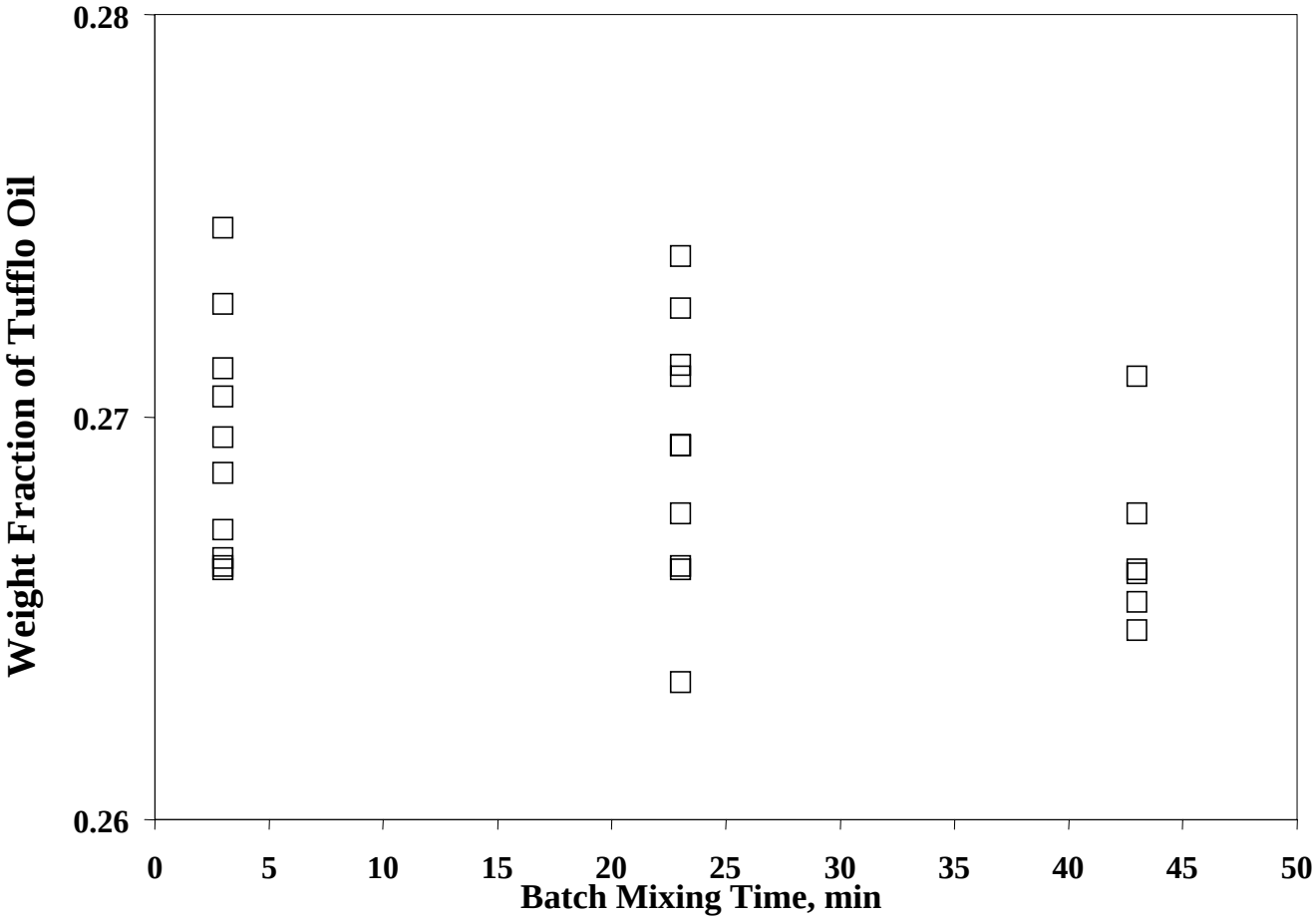


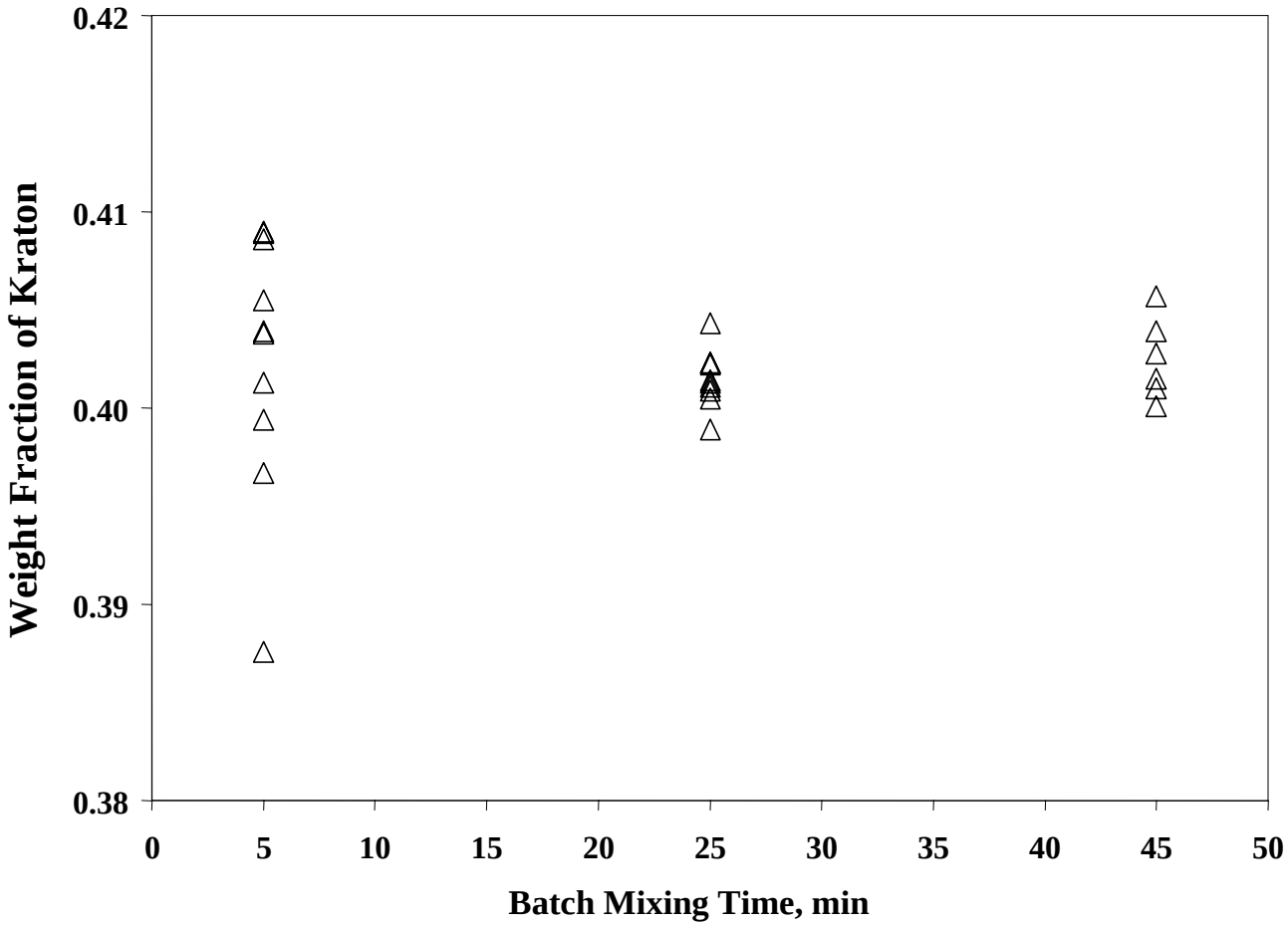
The deconvolution of the diffraction pattern of the conductive composite

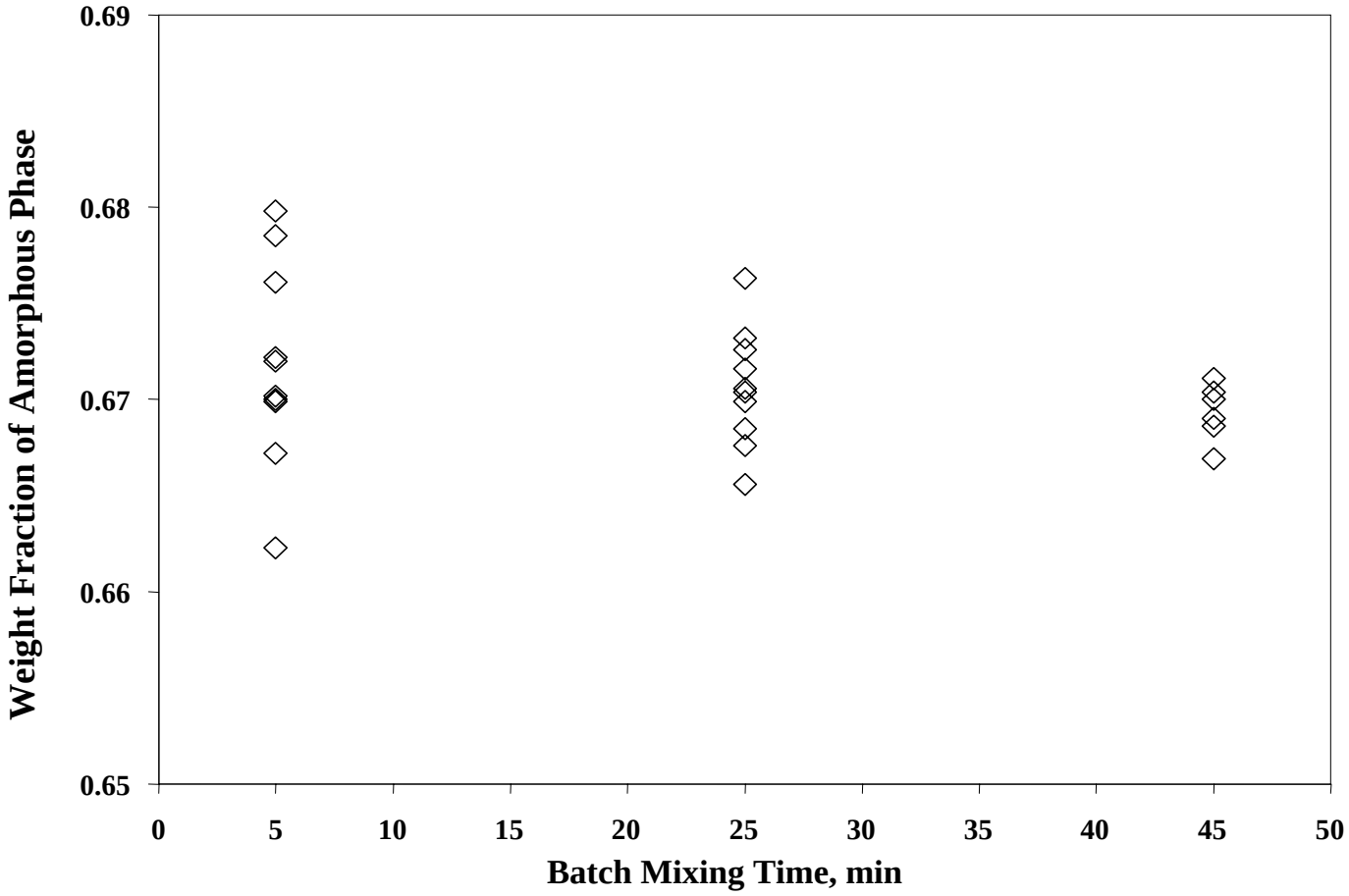


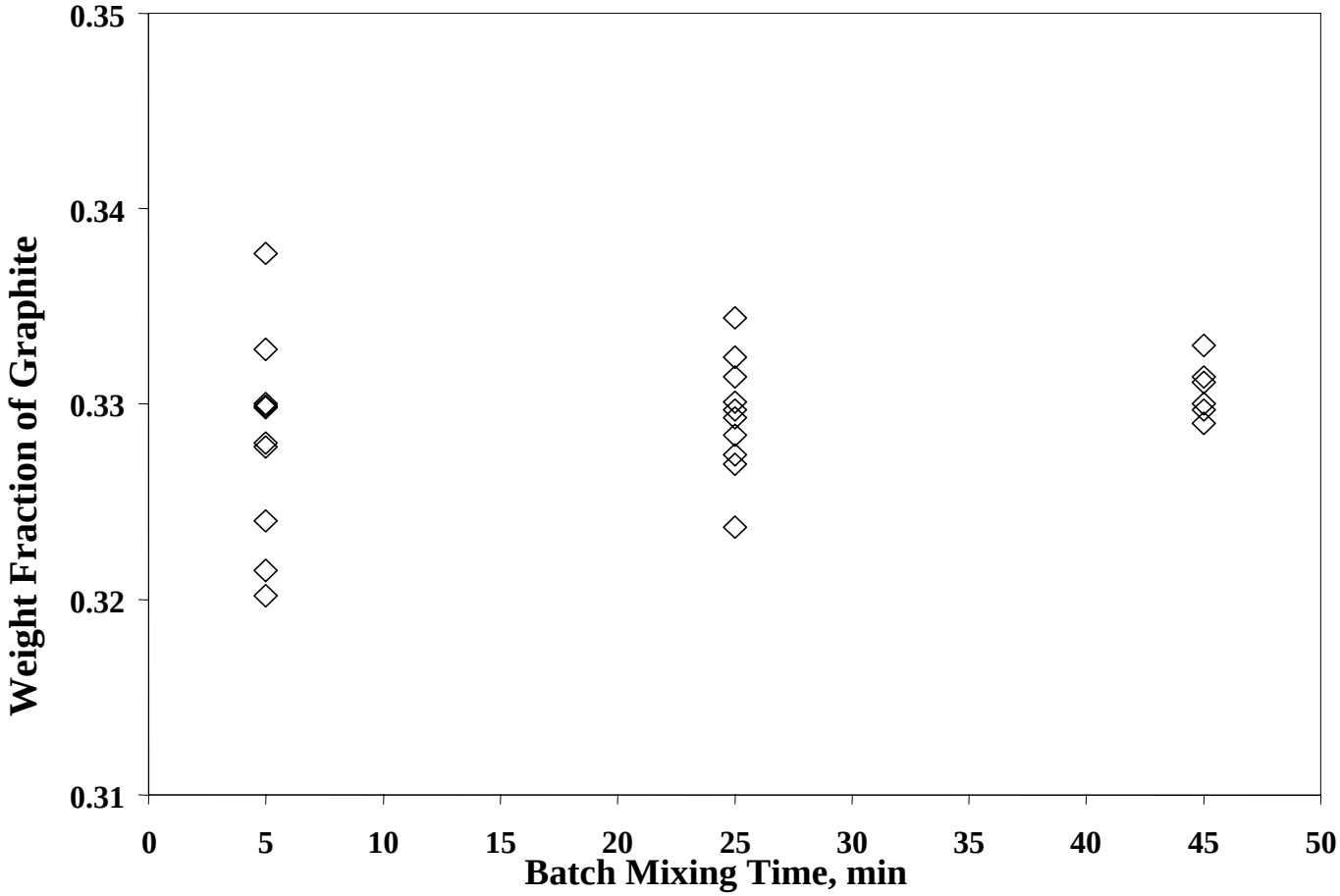
Determination of the concentrations of plasticizer, elastomer and the graphite particles using TGA

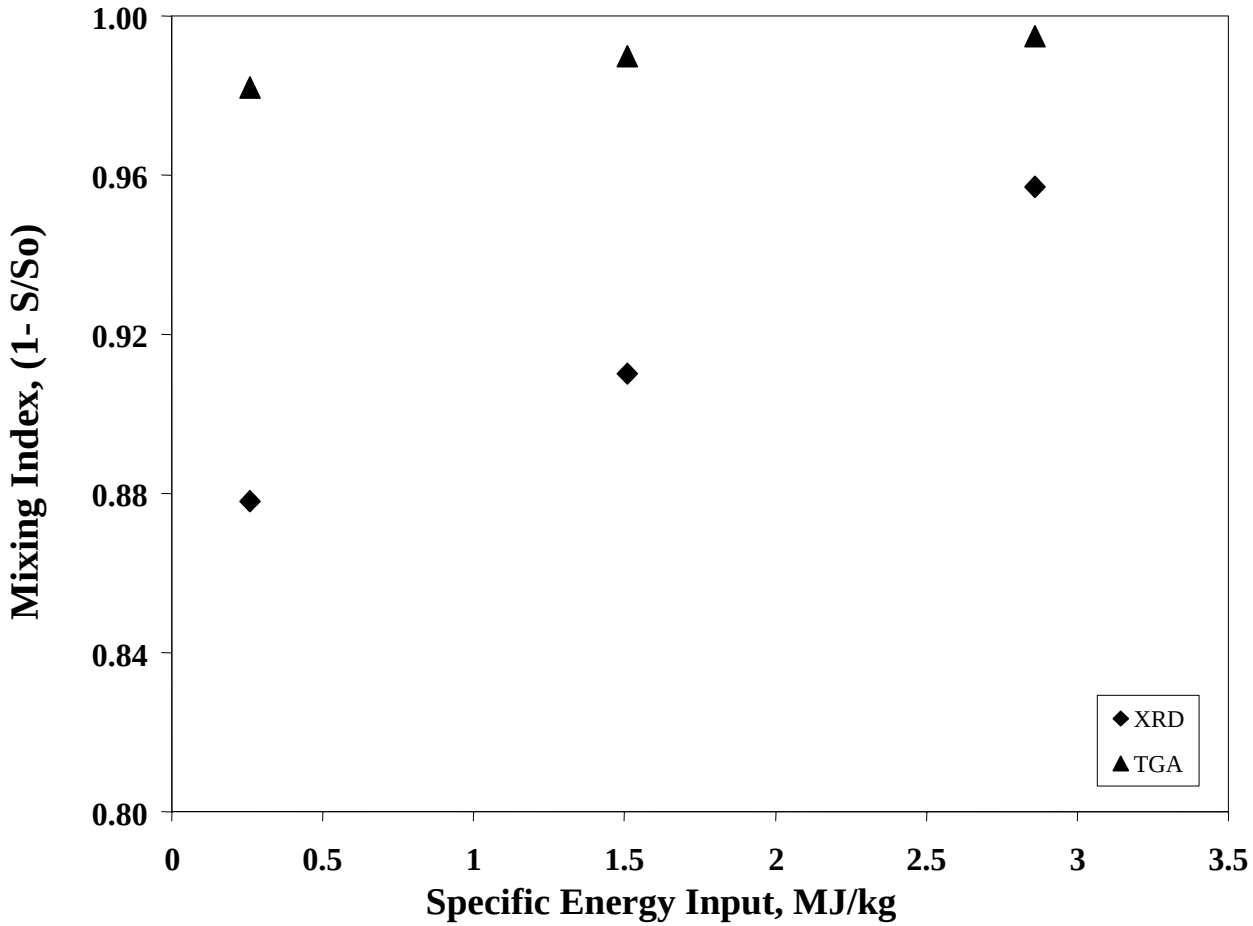

Specific Energy Input, MJ/kg
3.5
3
2.5
2
1.5
1
0.5
0
0
5
10
15
20
25
30
35
40
45
50
Batch Mixing Time, min

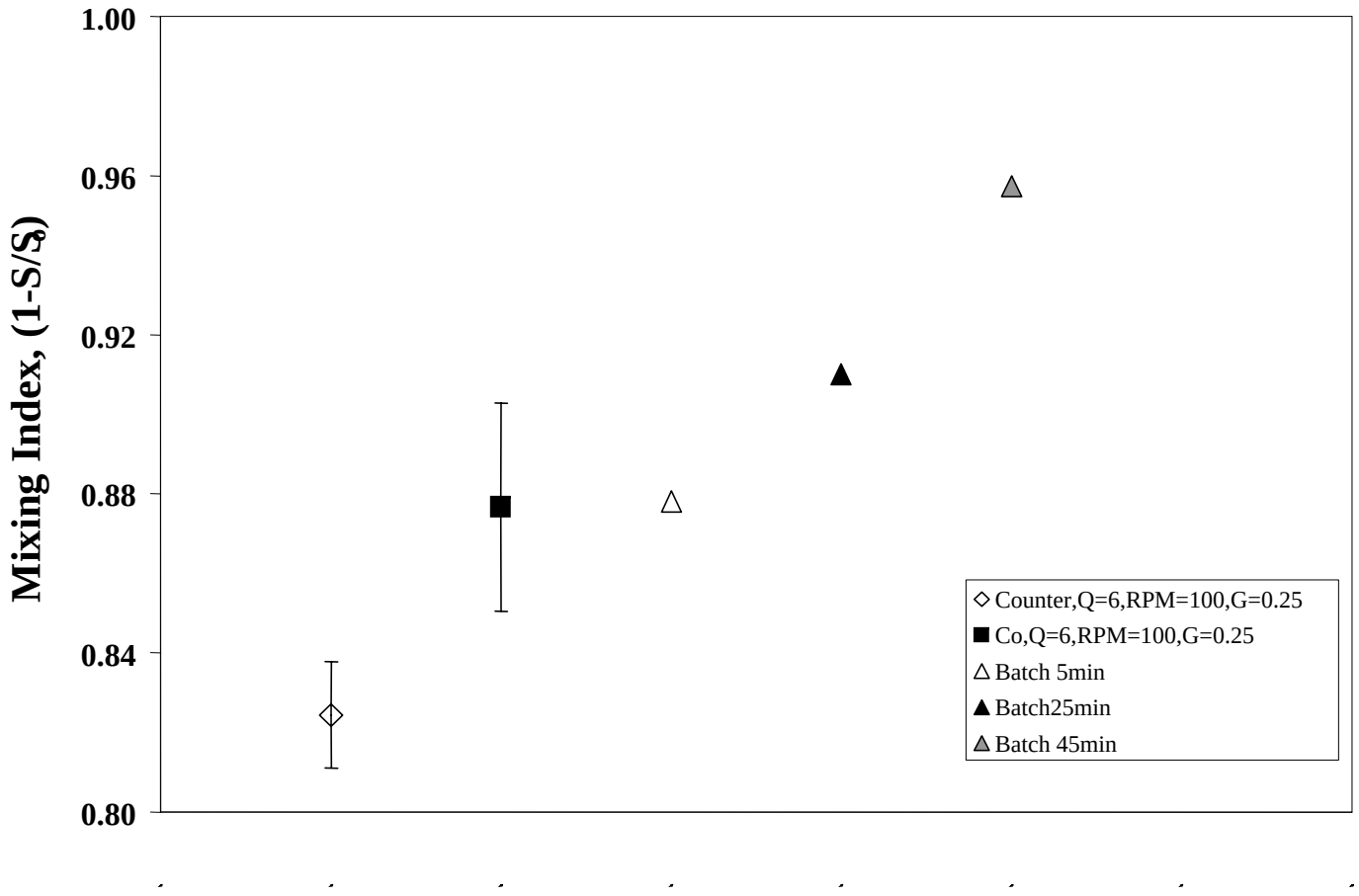

0.28
0.27
0.26
Weight Fraction of Tufflo Oil
0
5
10
15
20
25
30
35
40
45
50
Batch Mixing Time, min

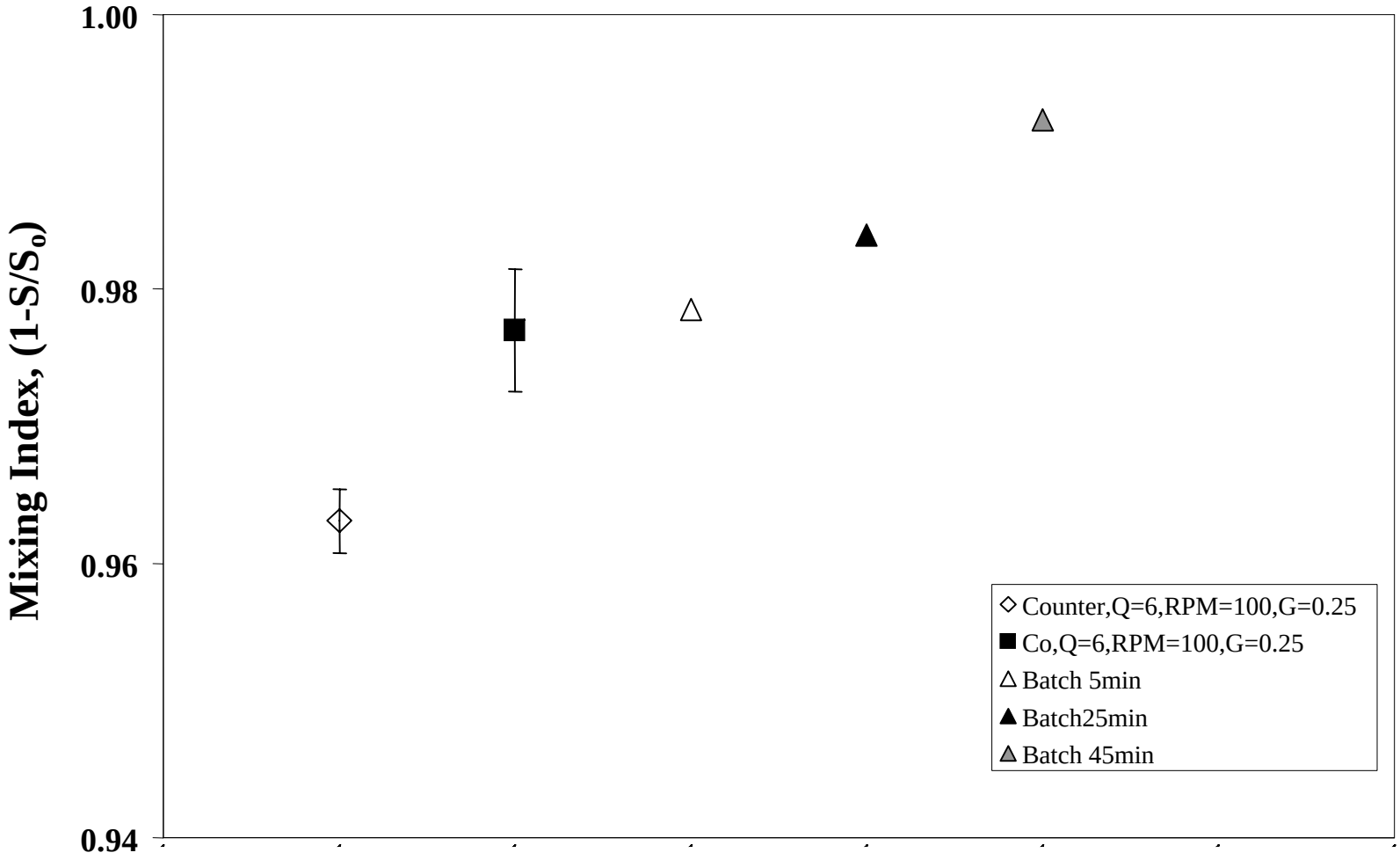

0.42
0.41
0.40
0.39
0.38
Weight Fraction of Kraton
0
5
10
15
20
25
30
35
40
45
50
Batch Mixing Time, min

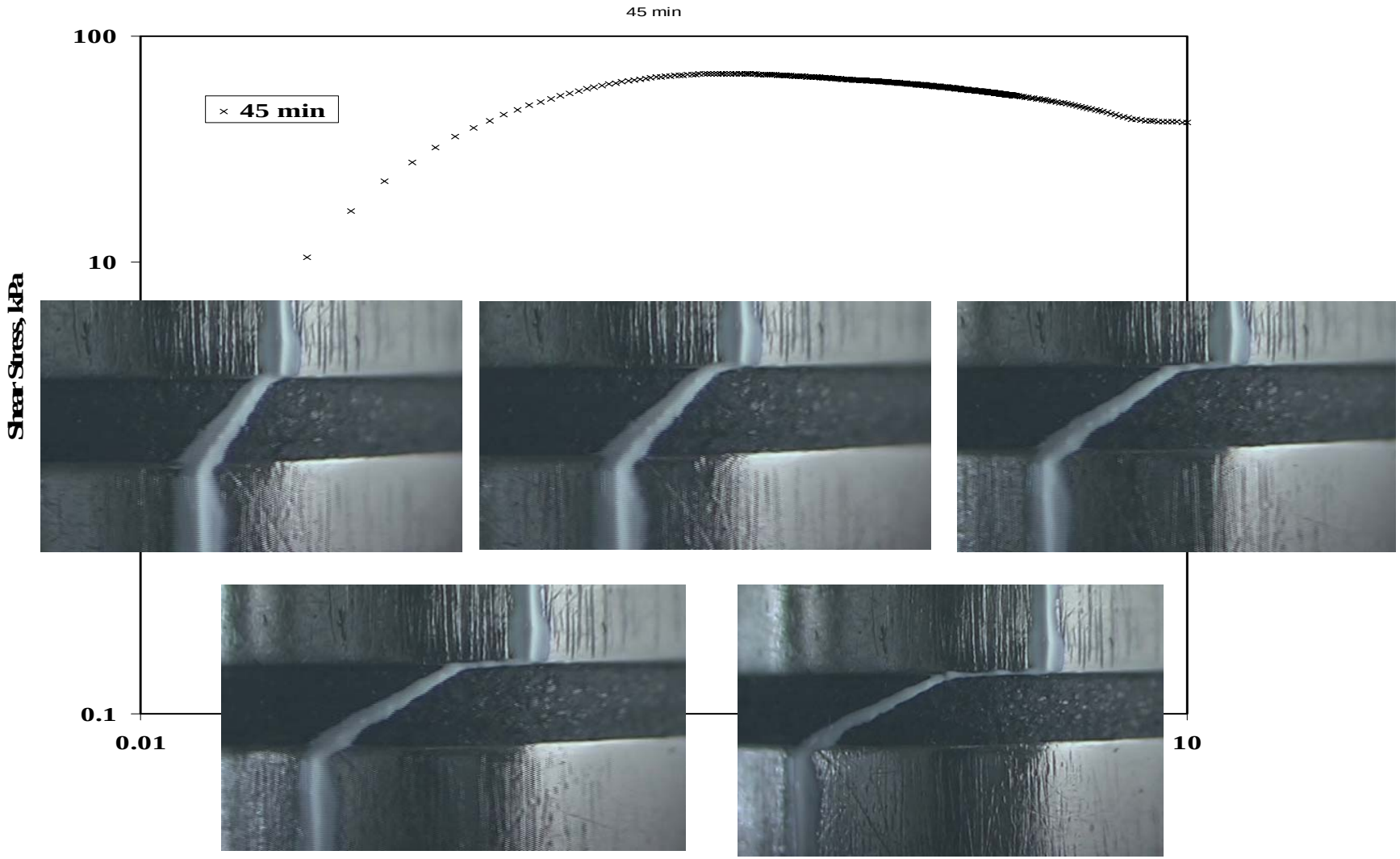

0.69
0.68
0.67
0.66
0.65
Weight Fraction of Amorphous Phase
0
5
10
15
20
25
30
35
40
45
50
Batch Mixing Time, min


0.35
0.34
0.33
0.32
0.31
Weight Fraction of Graphite
0
5
10
15
20
25
30
35
40
45
50
Batch Mixing Time, min

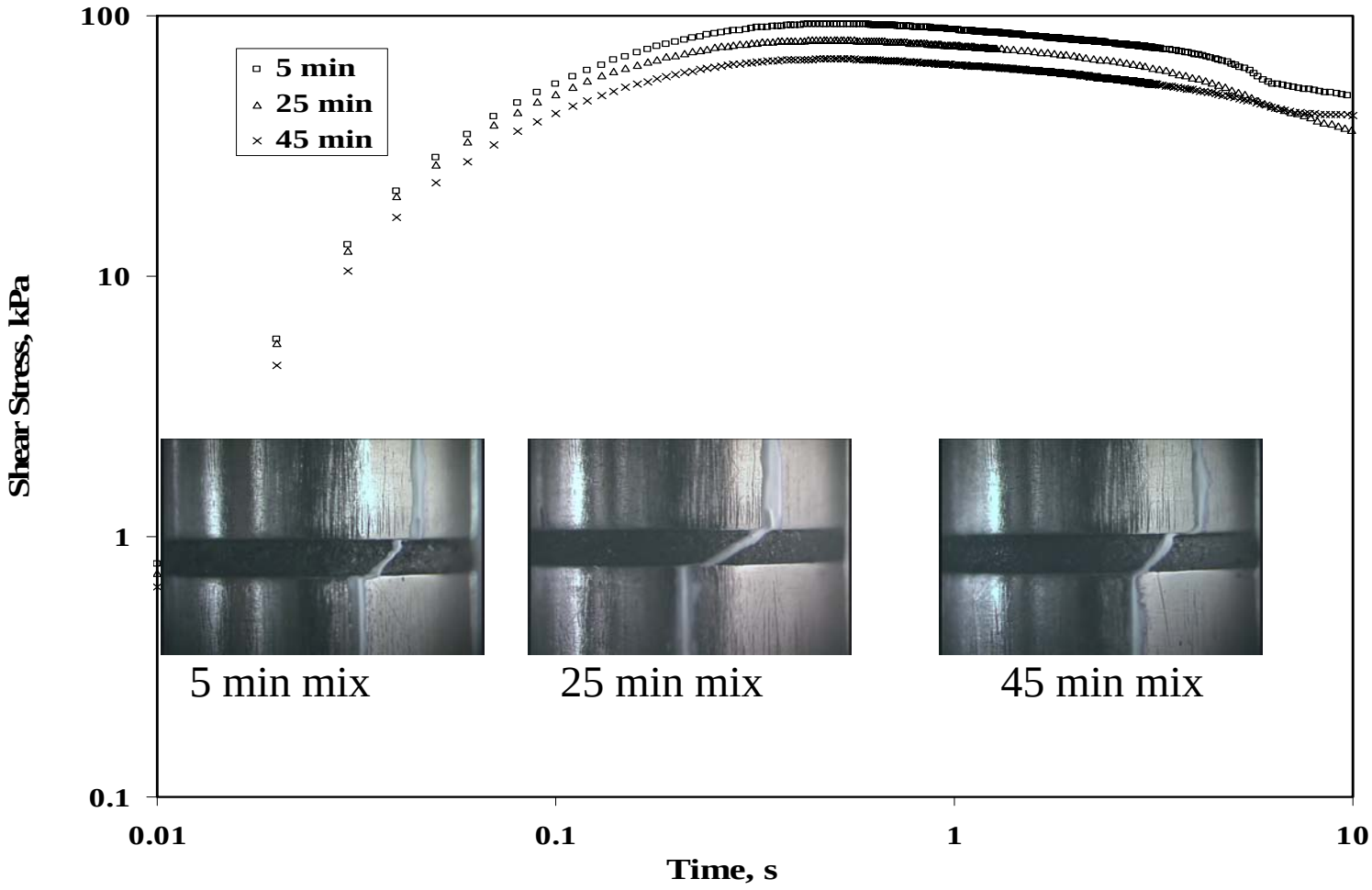

1.00
0.96
0.92
0.88
0.84
0.80
Mixing Index, (1- S/So)
0
0.5
1
1.5
2
2.5
3
3.5
Specific Energy Input, MJ/kg
XRD
TGA


1.00
0.96
0.92
0.88
0.84
0.80
Mixing Index, (1-S/S0)
Counter,Q=6,RPM=100,G=0.25
Co,Q=6,RPM=100,G=0.25
Batch 5min
Batch25min
Batch 45min

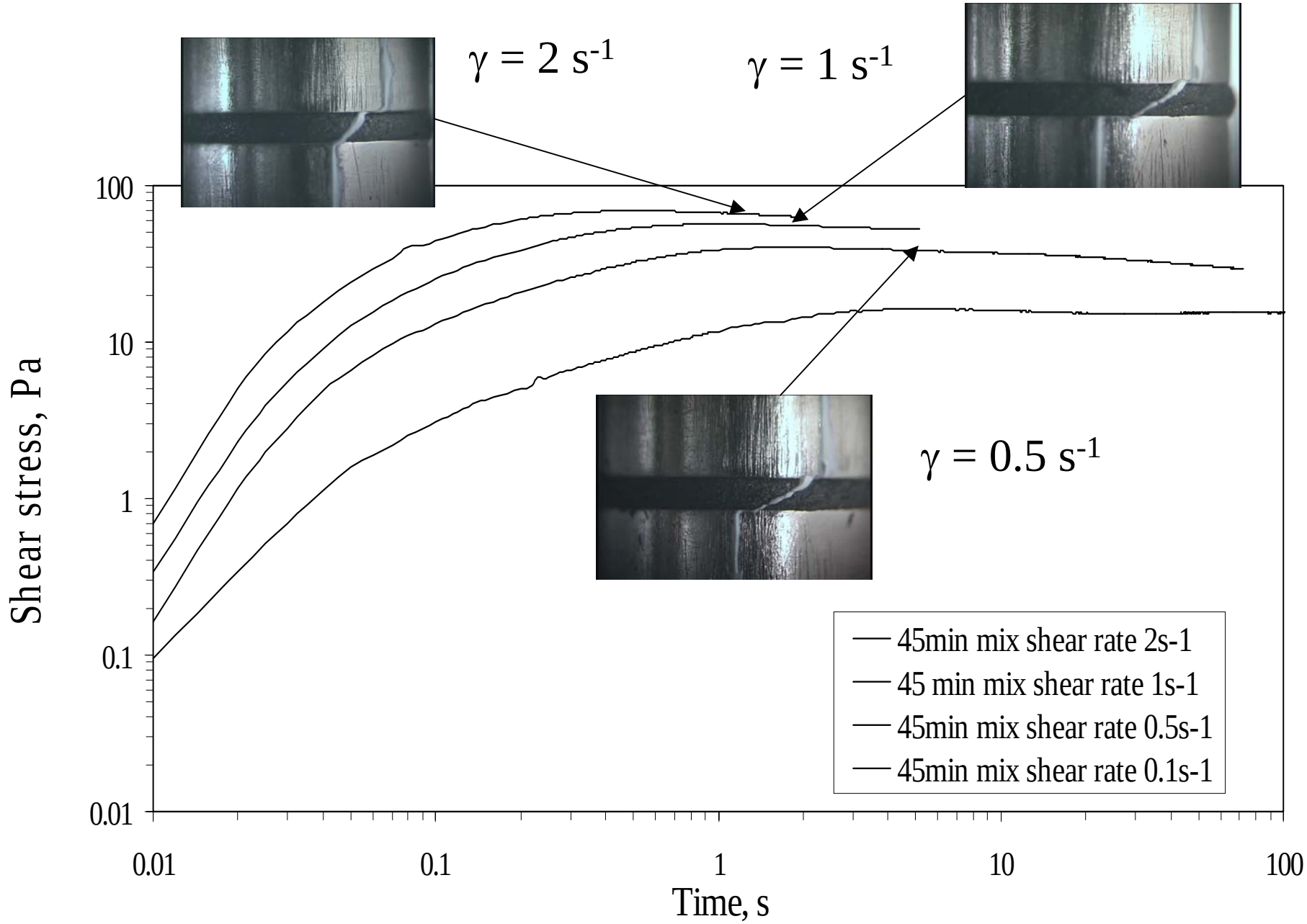

1.00
0.98
0.96
0.94
Mixing Index, (1-S/S$_o$)
Counter,Q=6,RPM=100,G=0.25
Co,Q=6,RPM=100,G=0.25
Batch 5min
Batch25min
Batch 45min

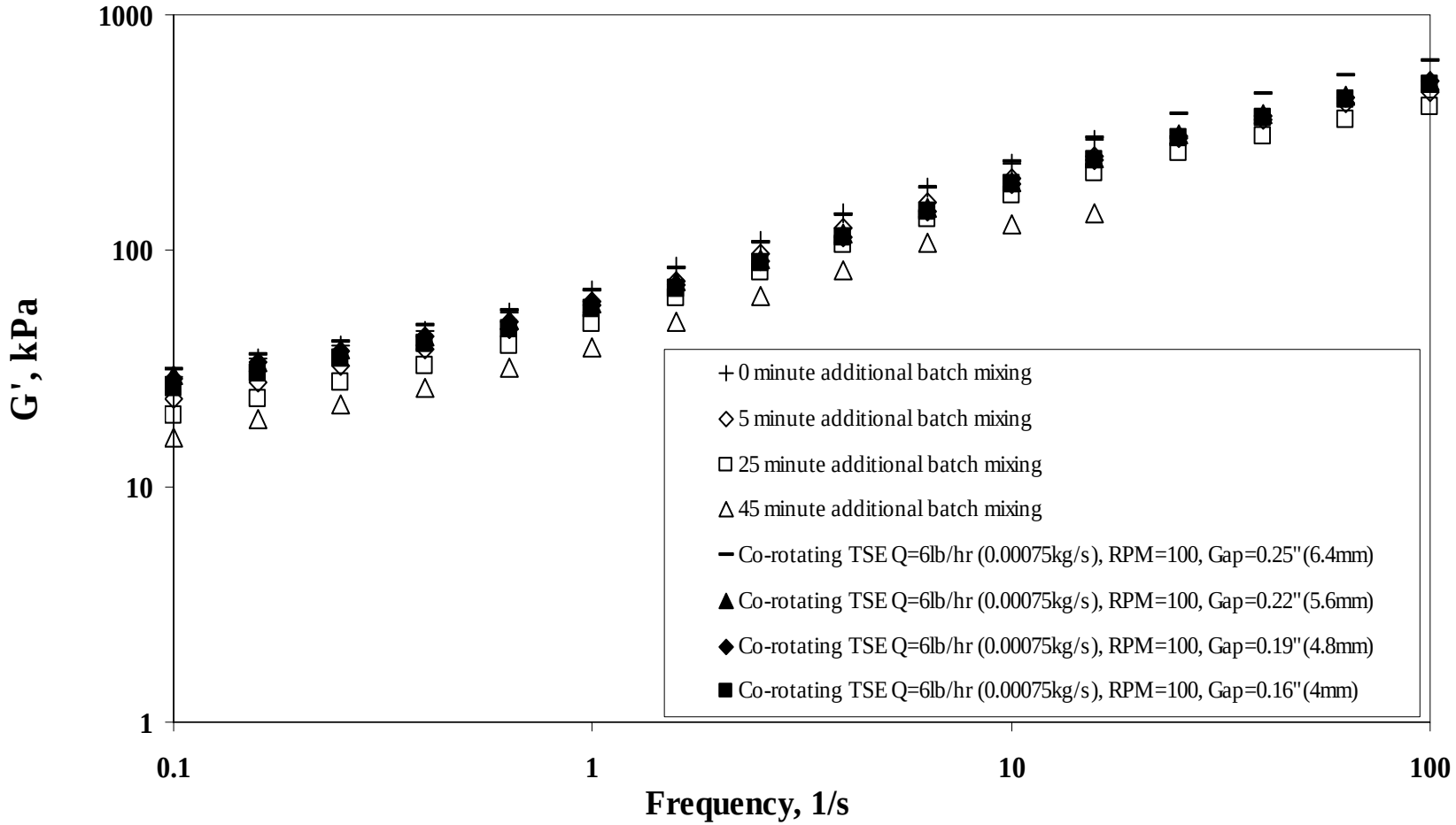


45 min mix

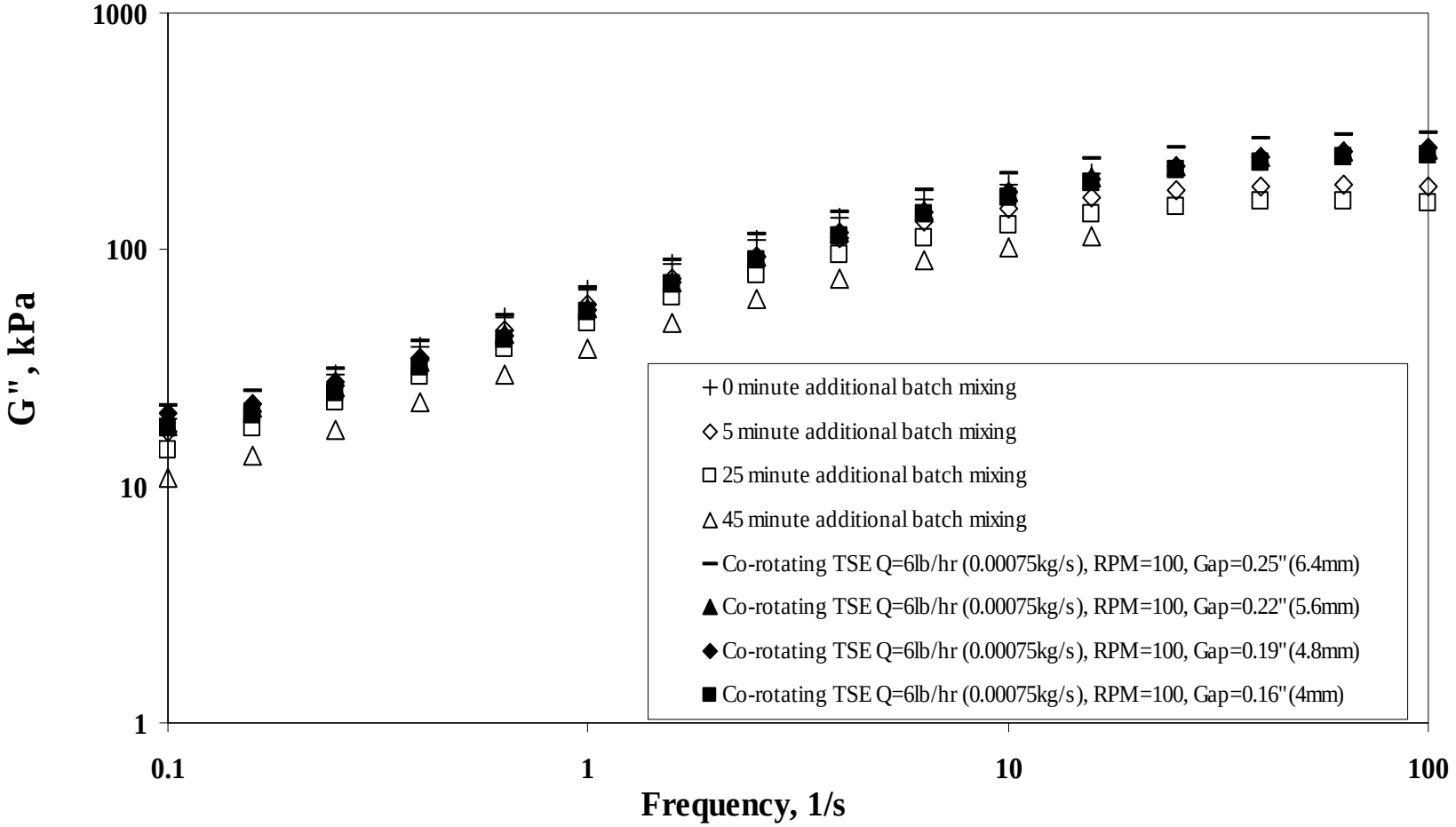


Comparison of slip behavior for 5, 25 and 45 minute batch mixed material at 2 s^{-1} and 95 ^{o}C

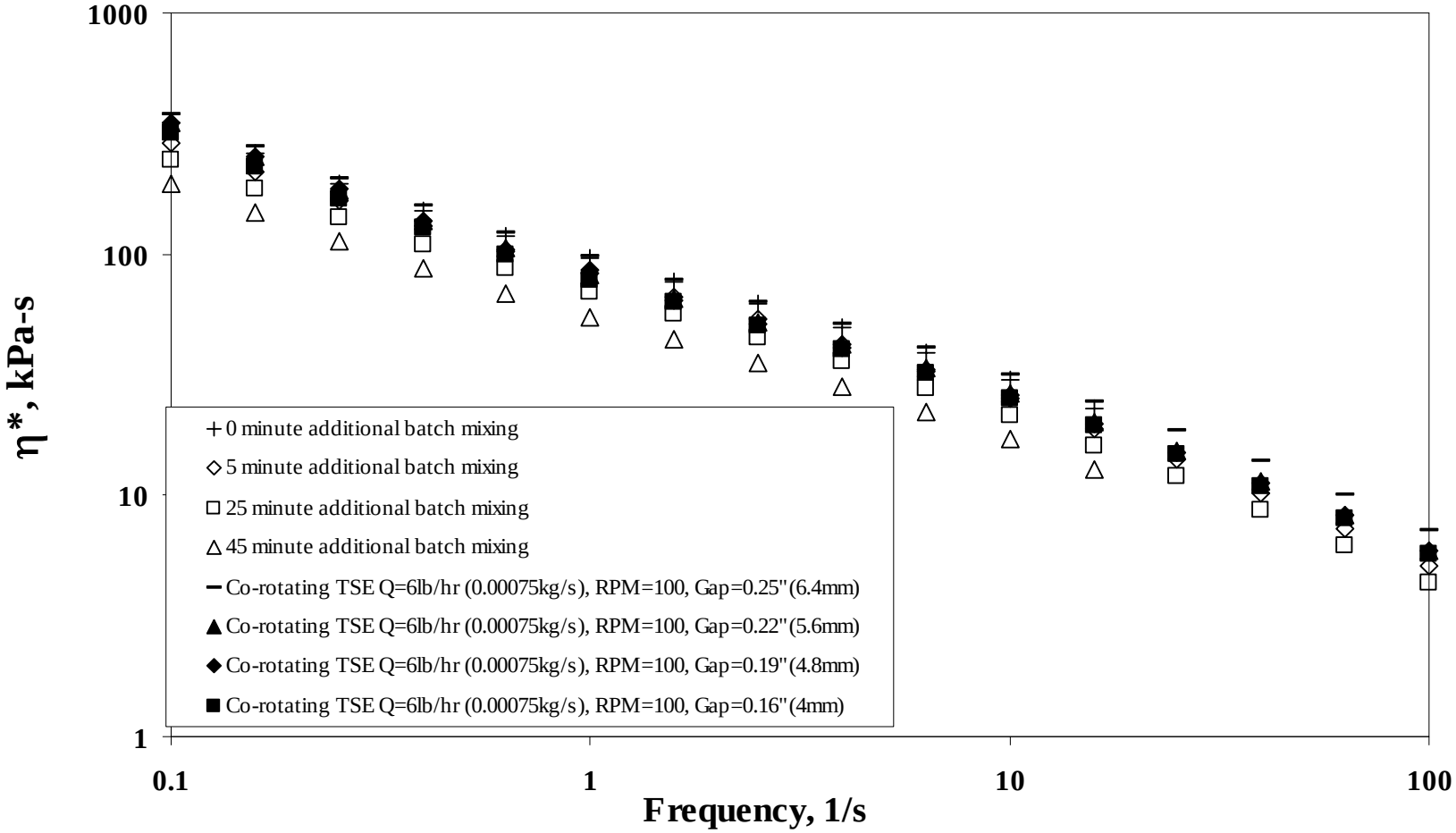

γ = 2 s-1
γ = 1 s-1
γ = 0.5 s-1
Shear stress, Pa
Time, s
100
10
1
0.1
0.01
0.01
0.1
1
10
100
45min mix shear rate 2s-1
45 min mix shear rate 1s-1
45min mix shear rate 0.5s-1
45min mix shear rate 0.1s-1



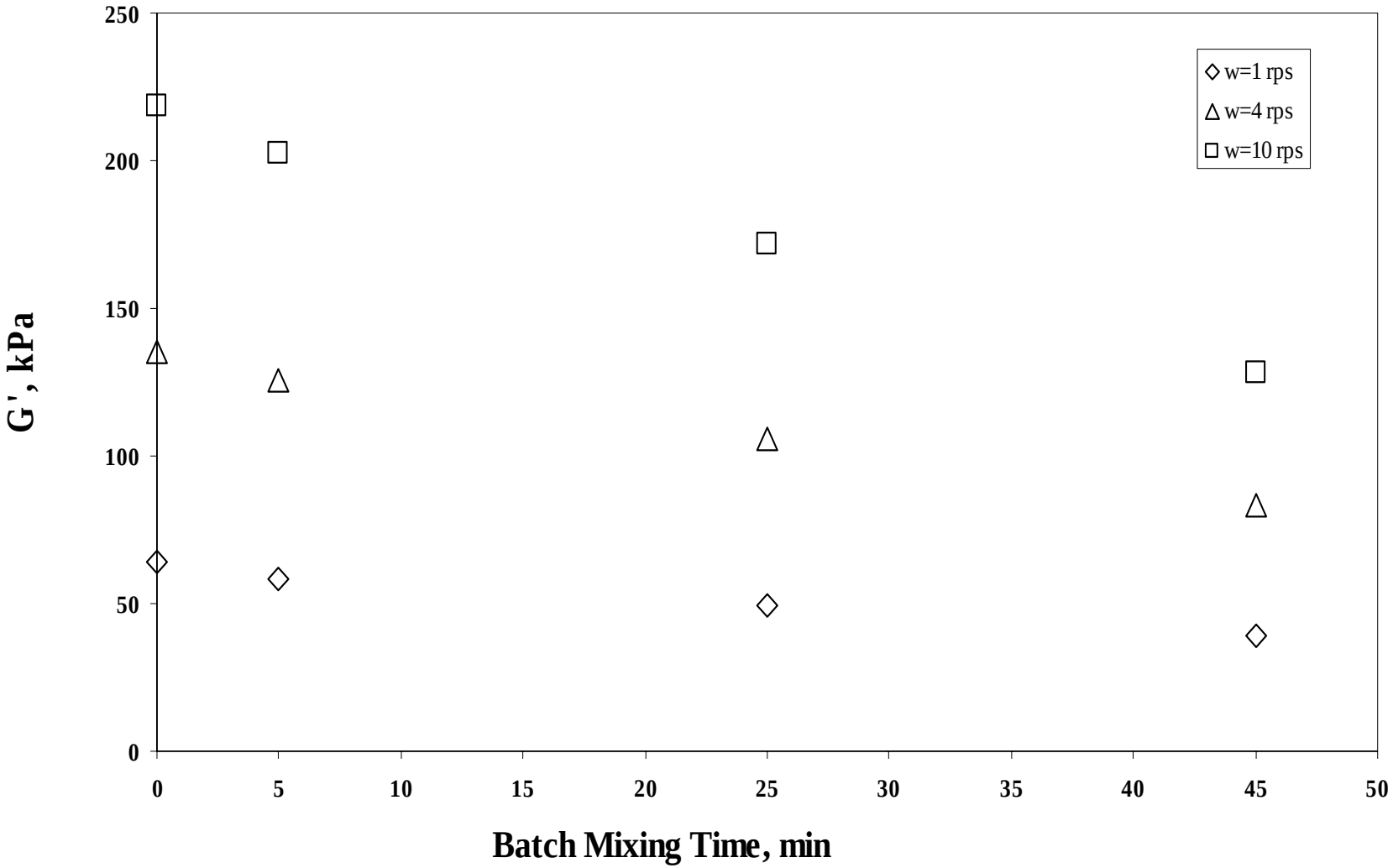
Storage modulus vs frequency plot for batch mixed and 6 lbs/hr (different slit die gaps) extruded samples



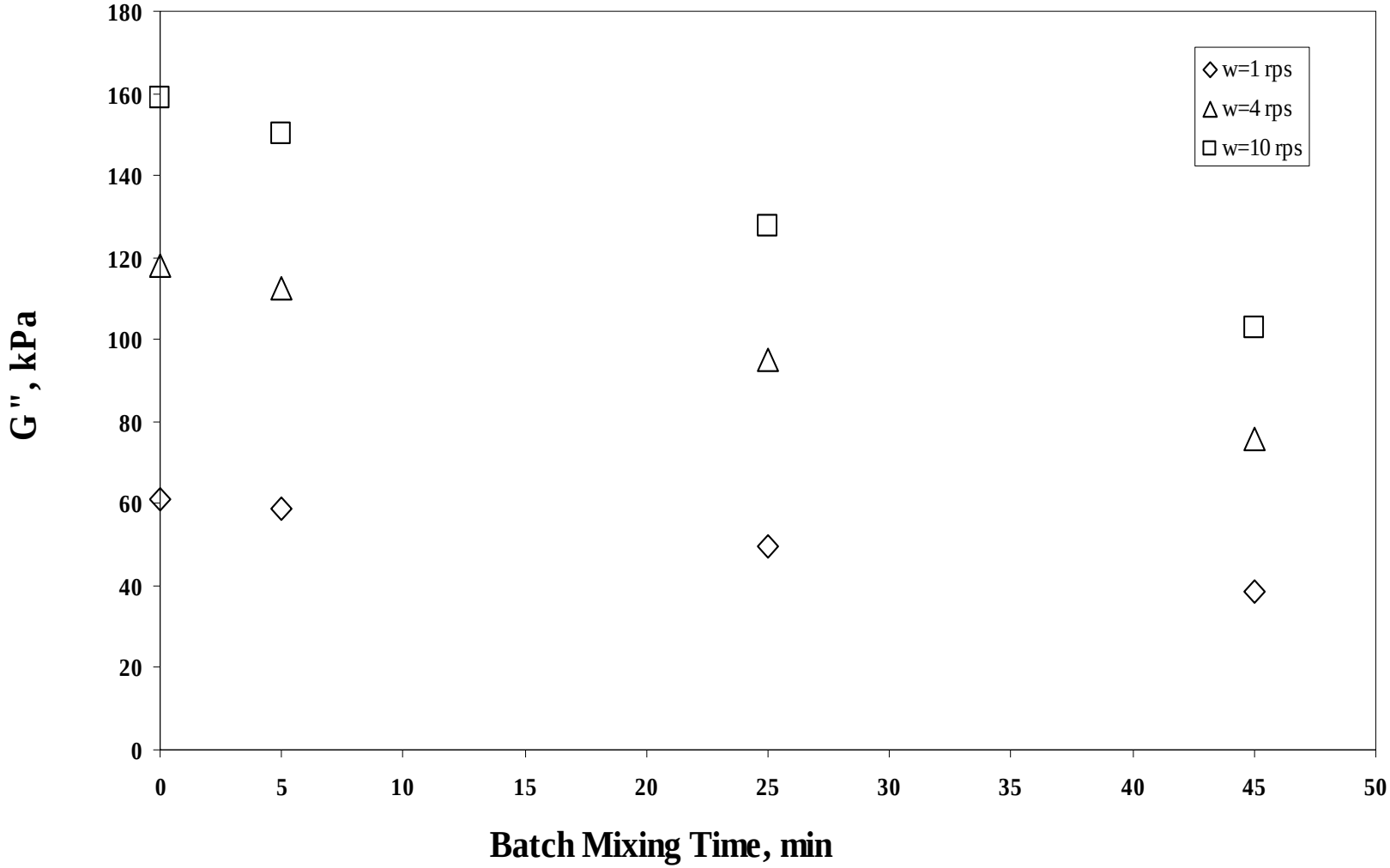
Loss modulus vs frequency plot for batch mixed and 6 lbs/hr (different slit die gaps) co-rotating twin screw extrusion samples



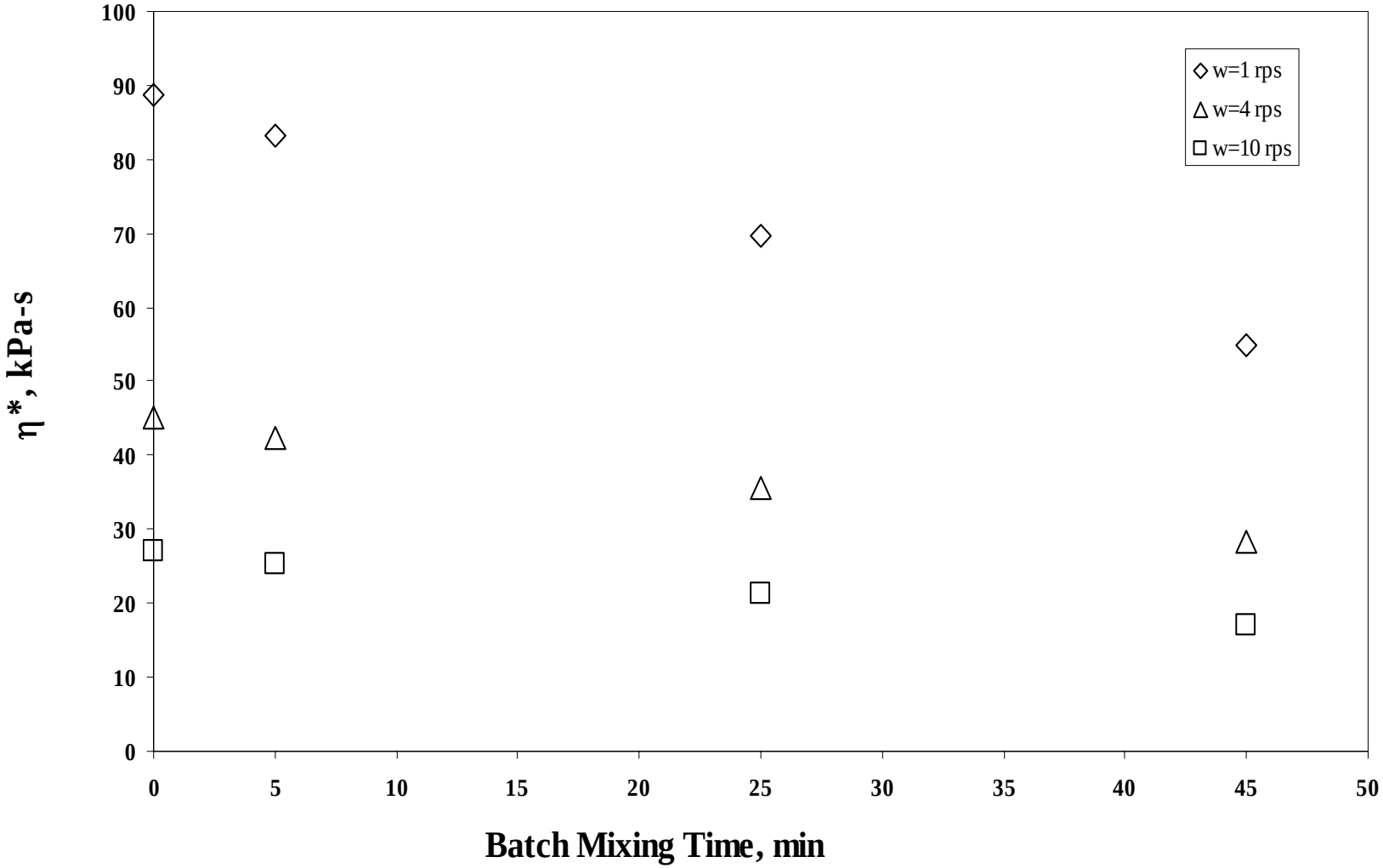
Magnitude of complex viscosity vs frequency plot for batch mixed and 6 lbs/hr (different slit die gaps) extruded samples



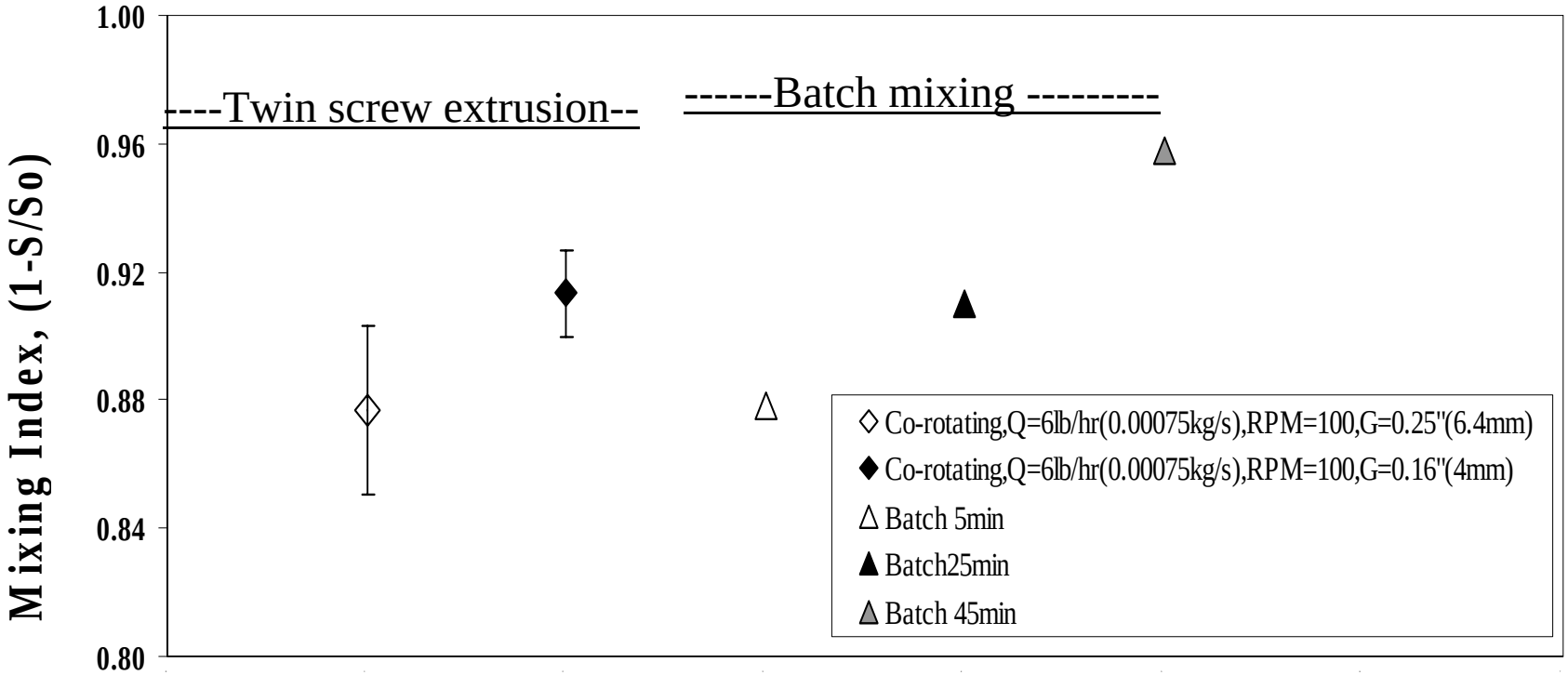
Storage modulus versus the additional batch mixing time at three frequencies



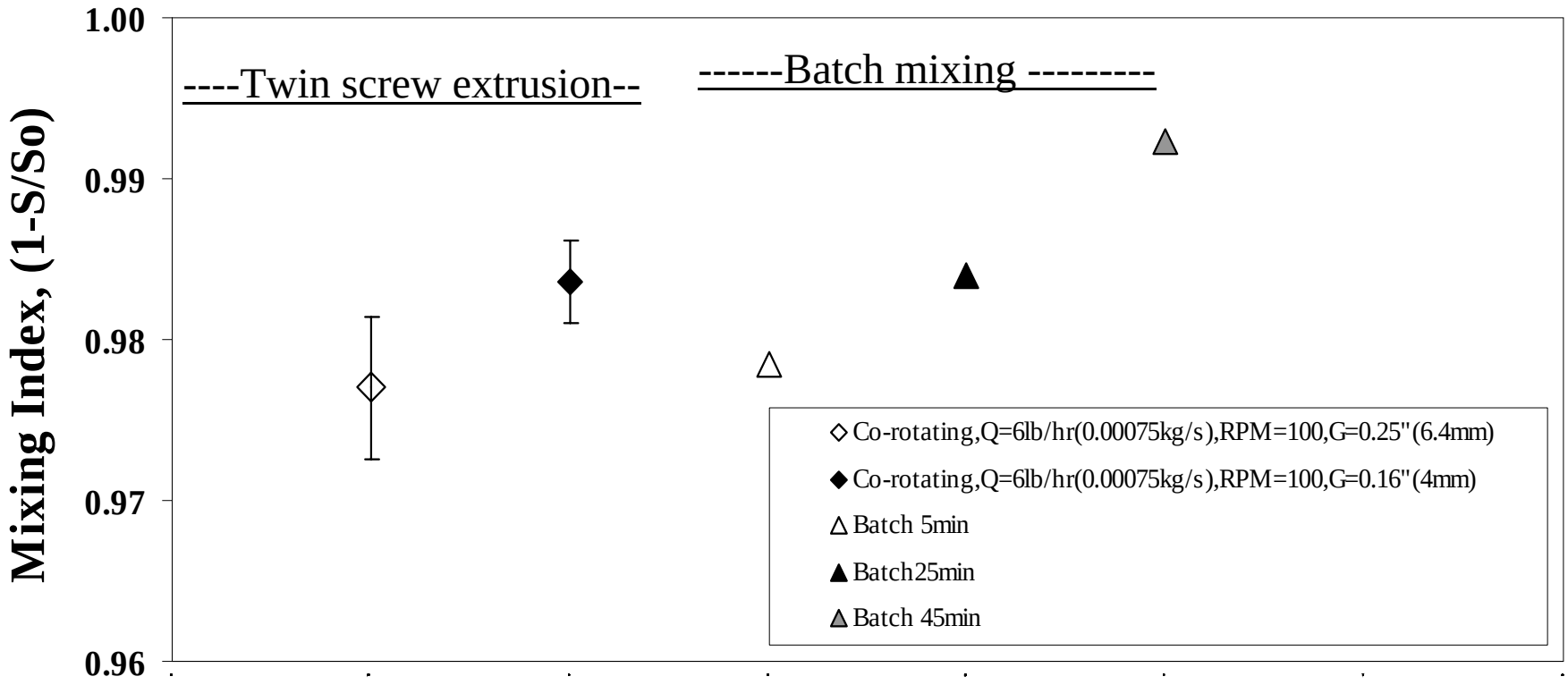
Loss modulus versus the additional batch mixing time at three frequencies



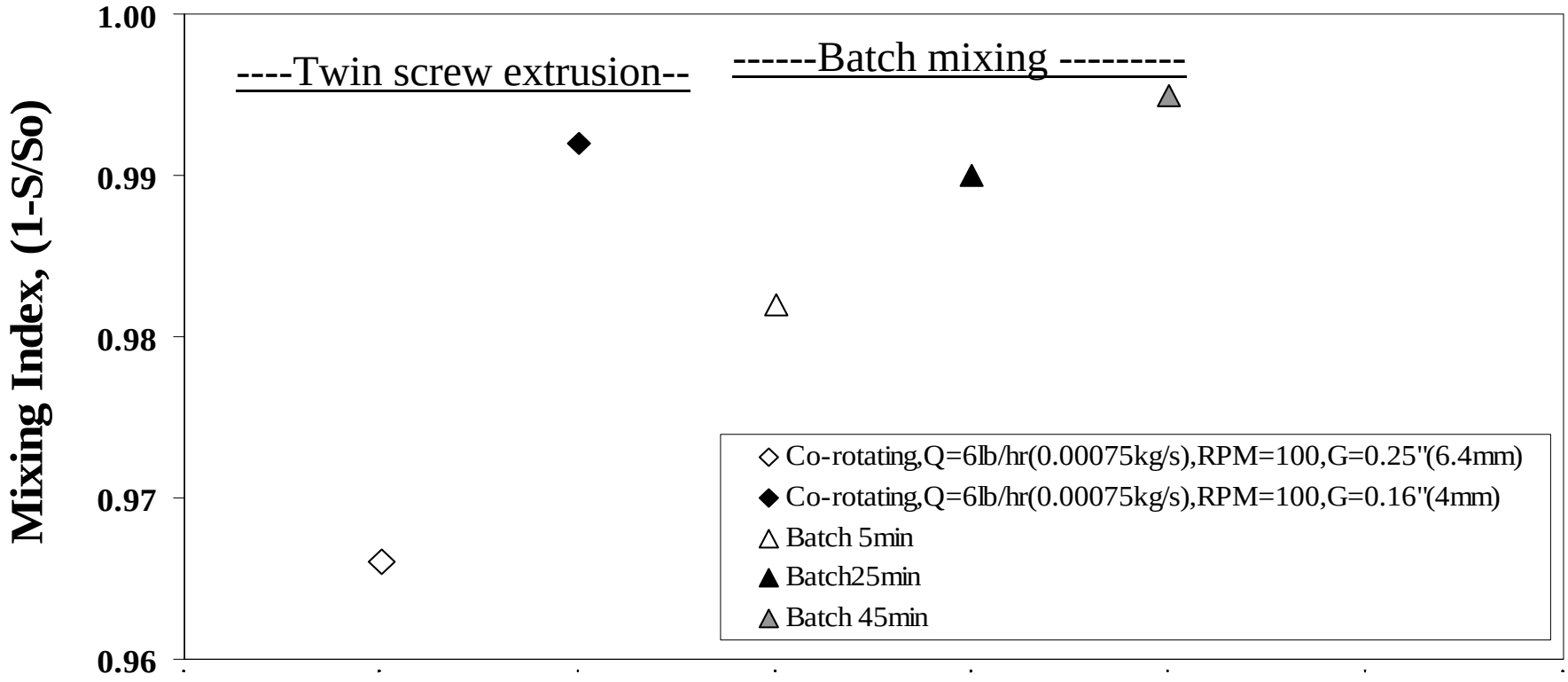
Magnitude of complex viscosity versus the additional batch mixing time at three frequencies



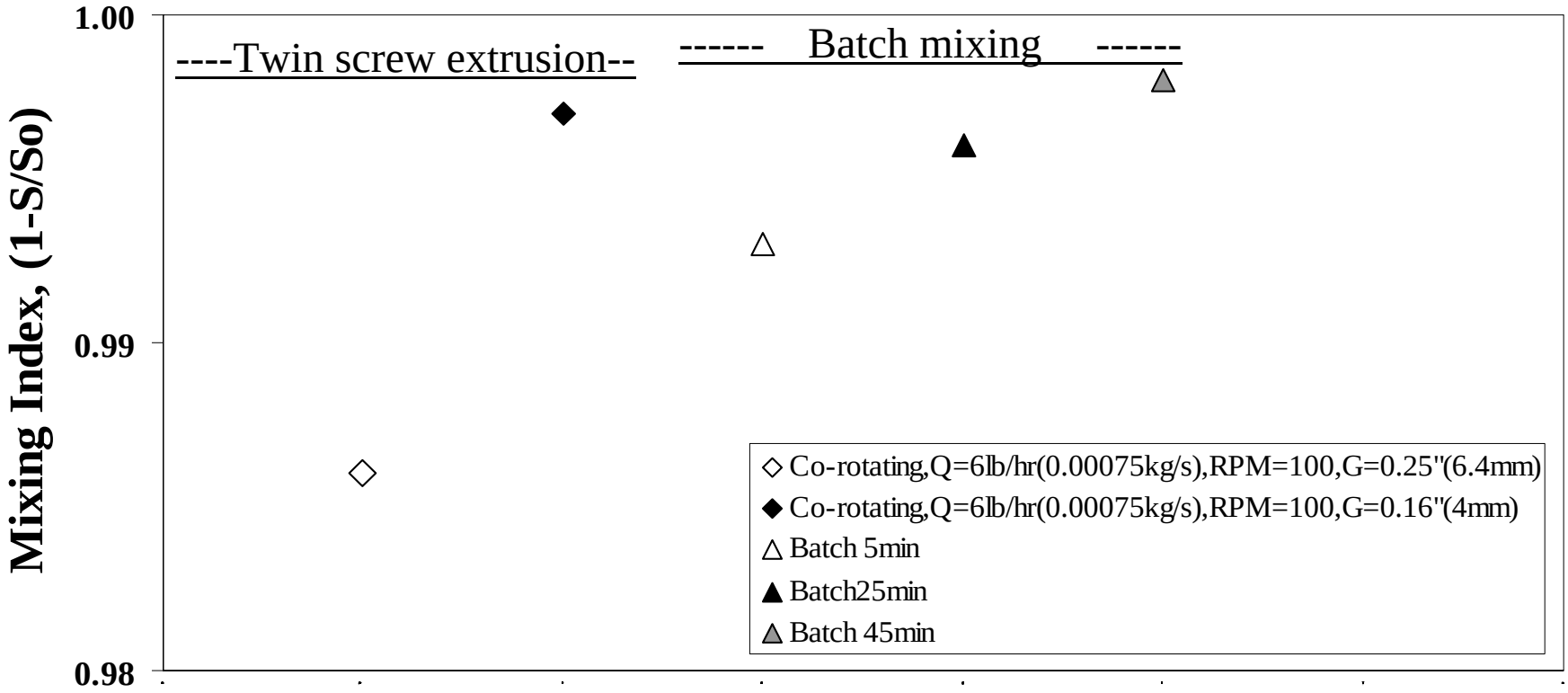
Mixing index for amorphous phase (from WXRD) values of specimens processed with the batch mixer and co-rotating twin screw extrusion



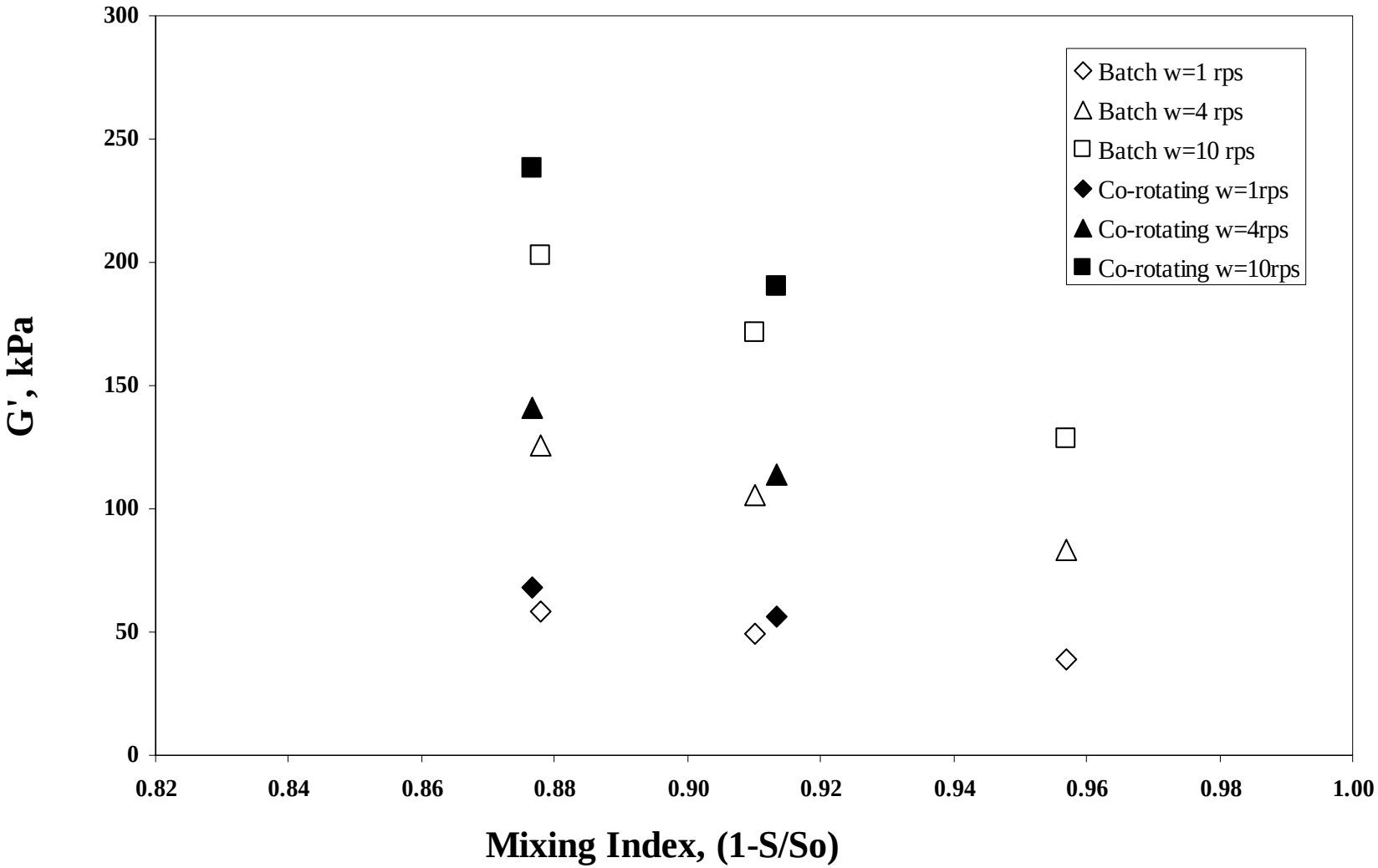
Mixing index for graphite phase (from WXRD) values of specimens processed with the batch mixer and co-rotating and counter-rotating twin screw extrusion



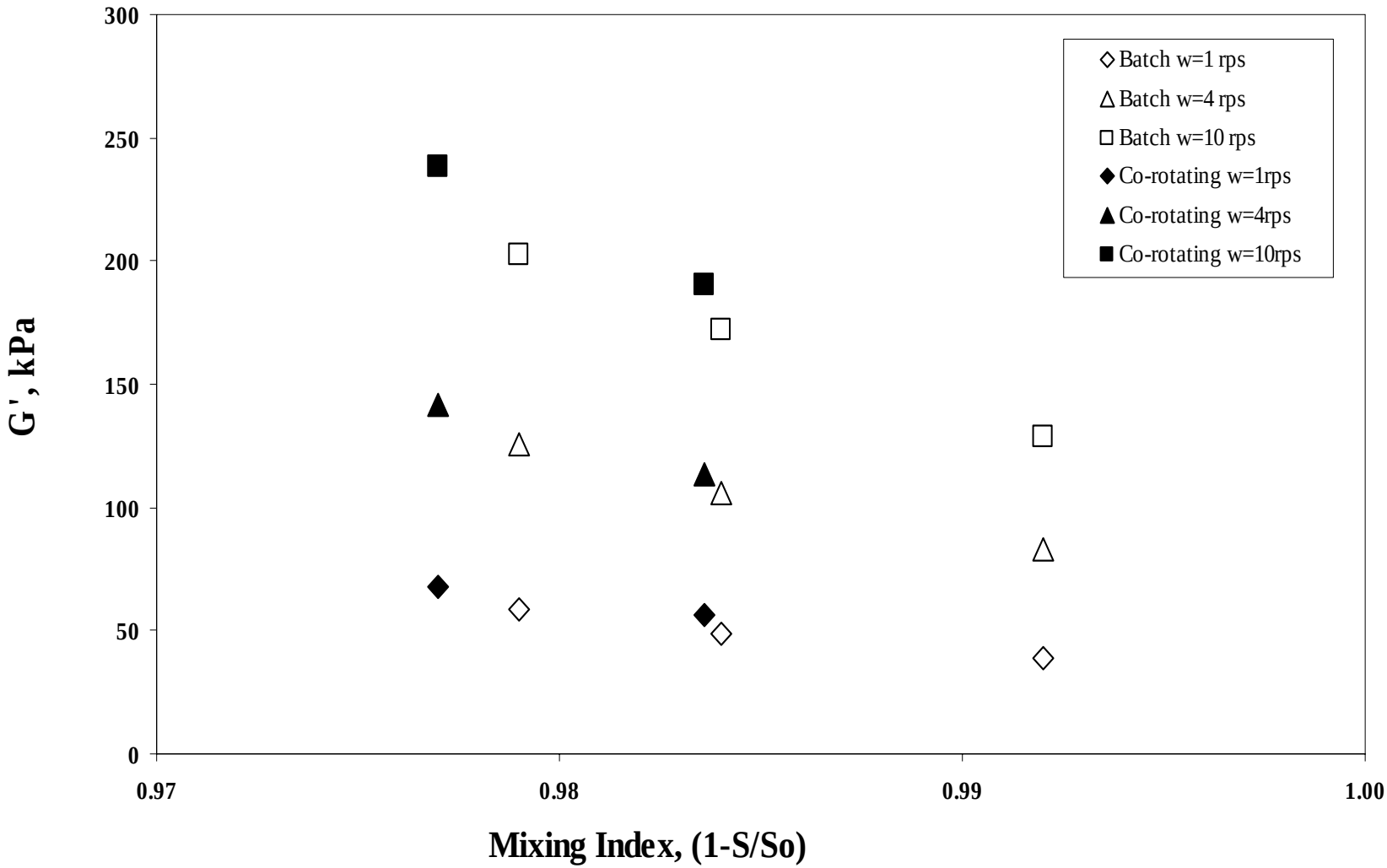
Mixing index for amorphous phase (from TGA) values of specimens processed with the batch mixer and co-rotating twin screw extrusion



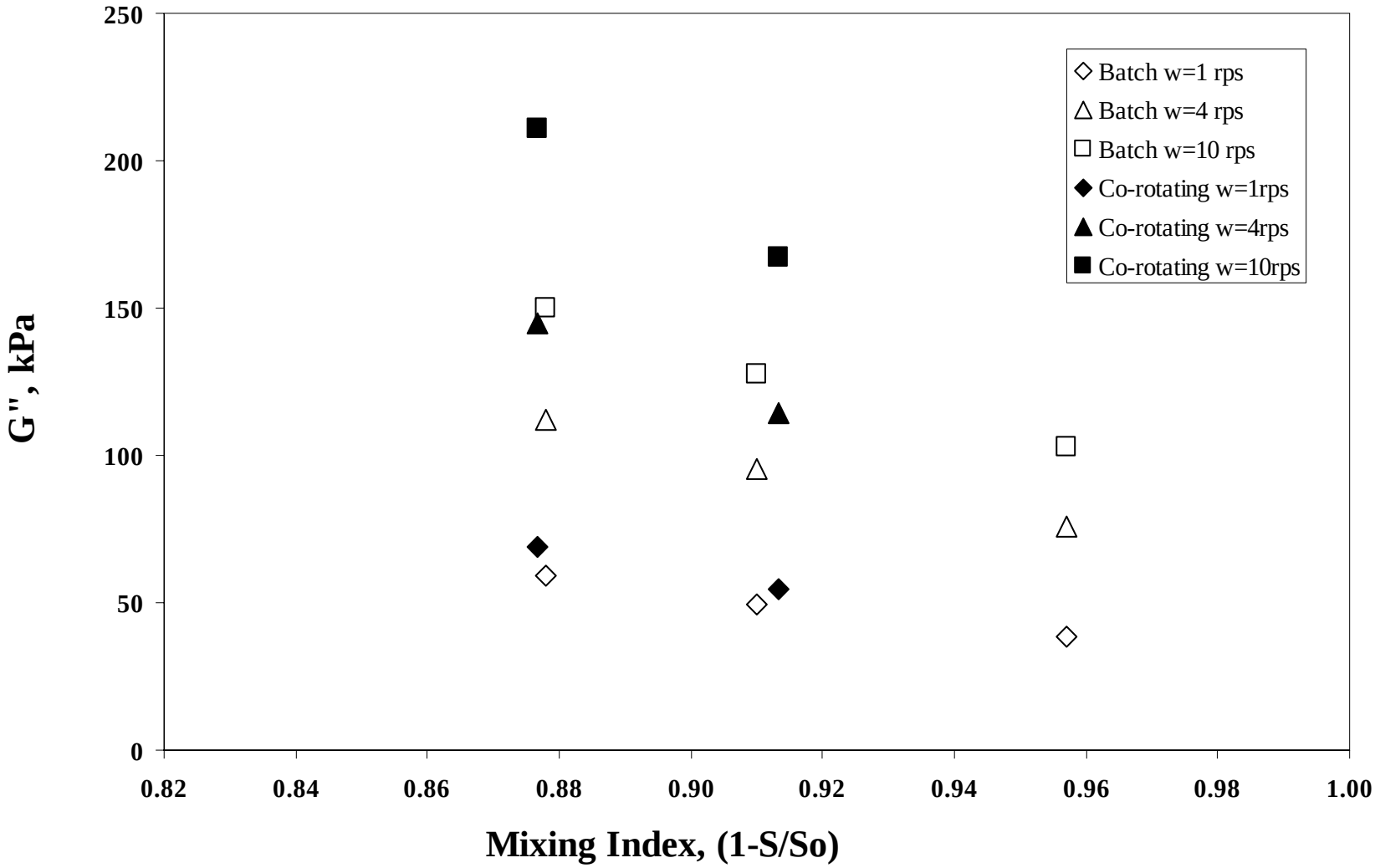
Mixing index for graphite phase (from TGA) values of specimens processed with the batch mixer and co-rotating and counter-rotating twin screw extrusion



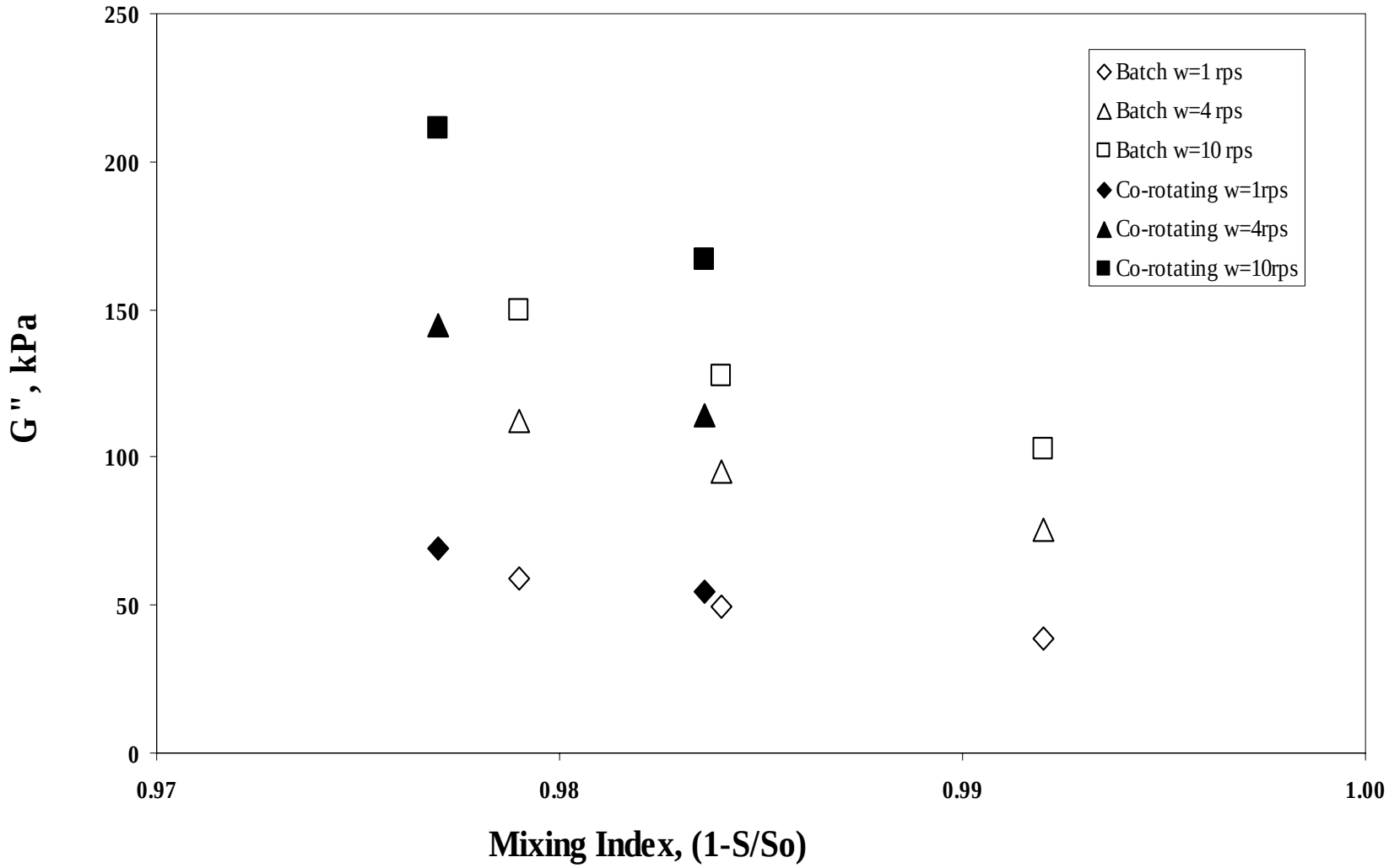
Storage modulus versus mixing index for amorphous phase (WXRD) at three frequencies



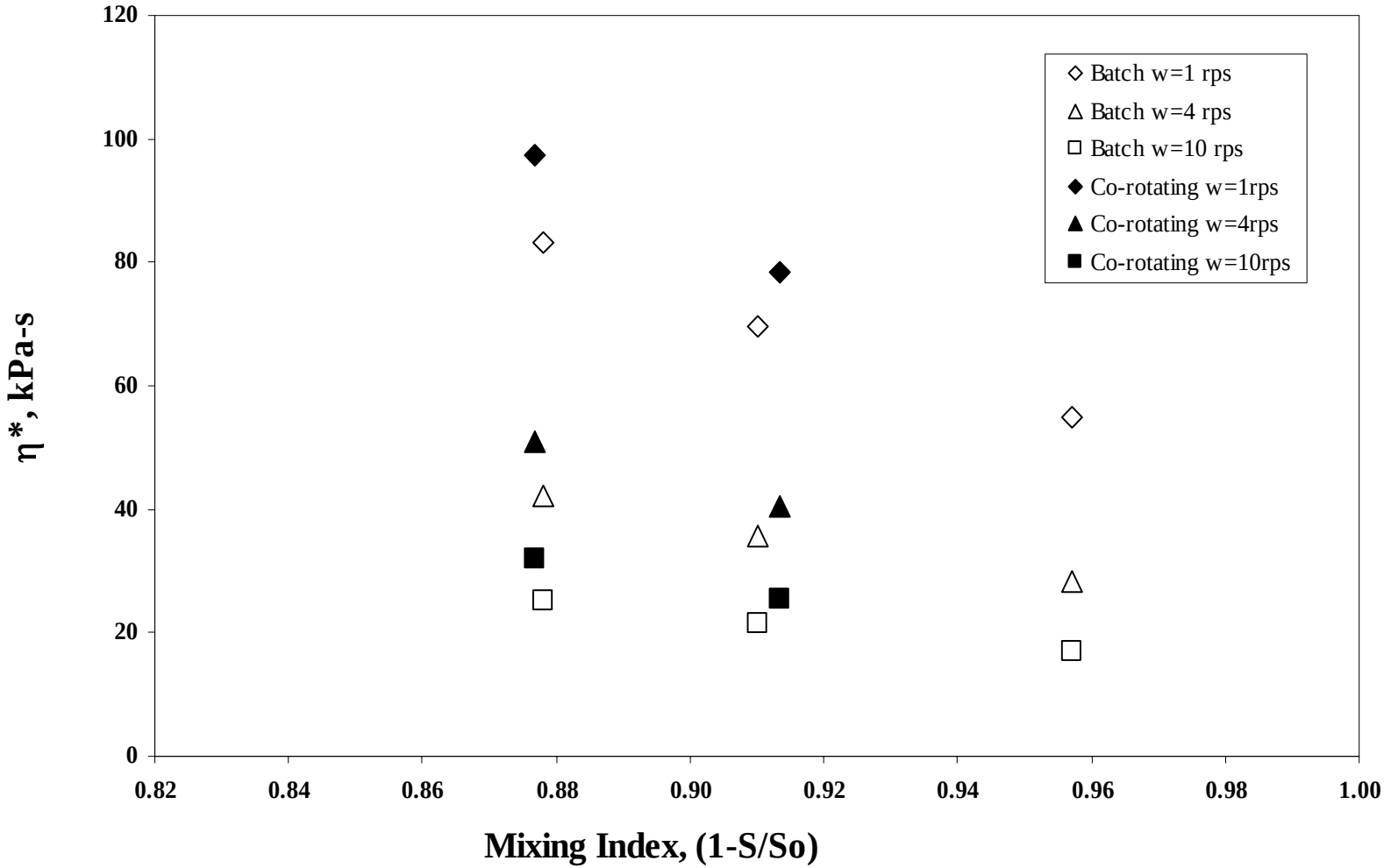
Storage modulus versus mixing index for graphite (WXRD) at three frequencies



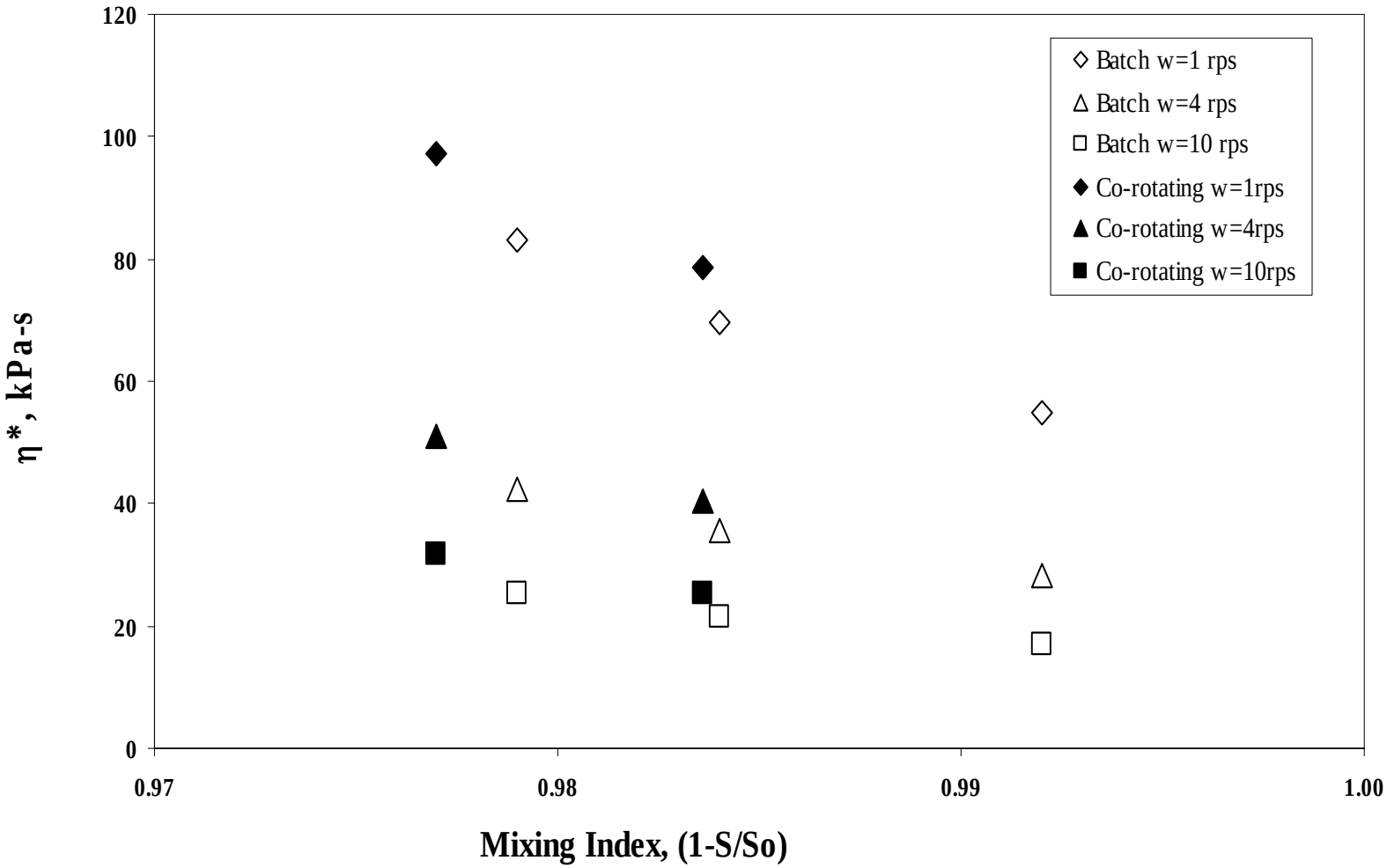
Loss modulus versus mixing index for amorphous phase (WXRD) at three frequencies



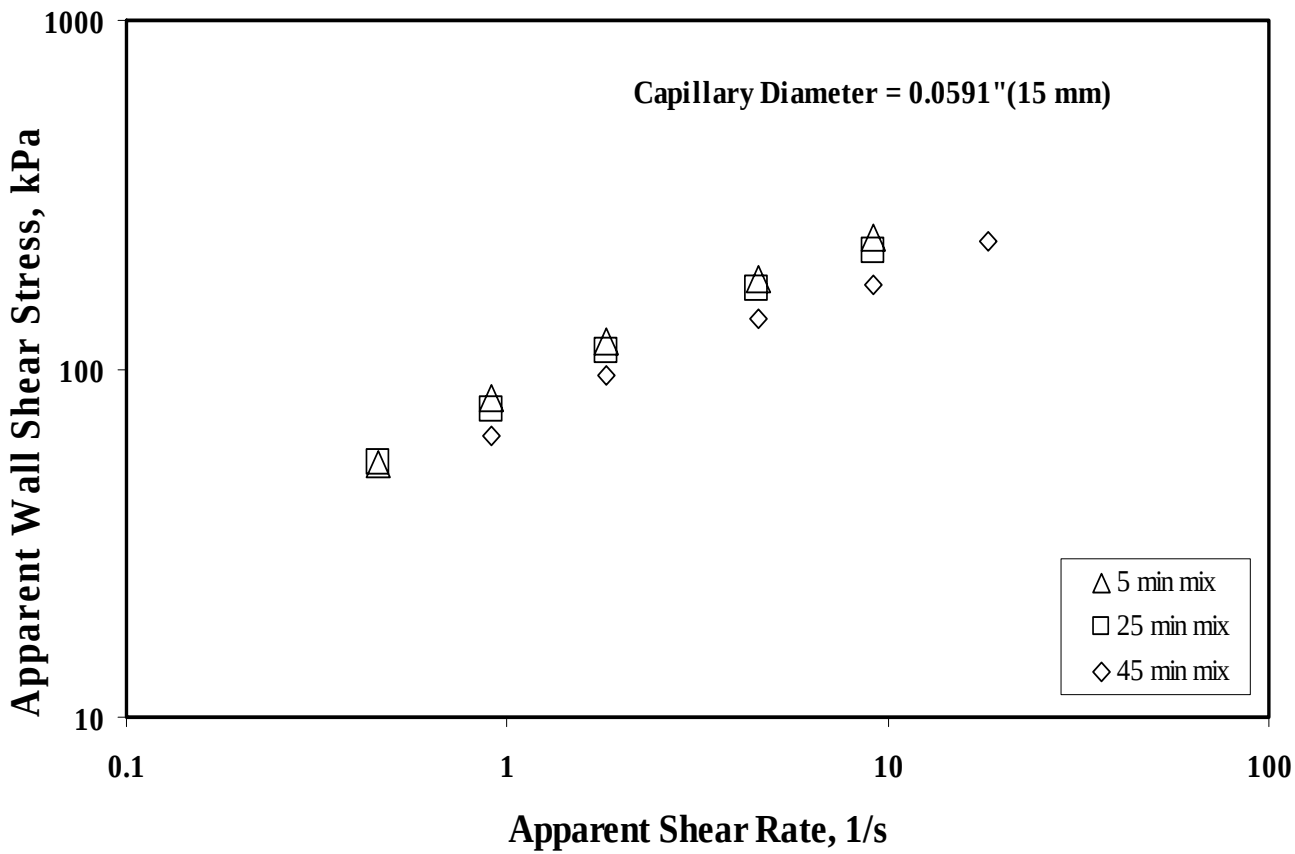
Loss modulus versus mixing index for graphite (WXRD) at three frequencies



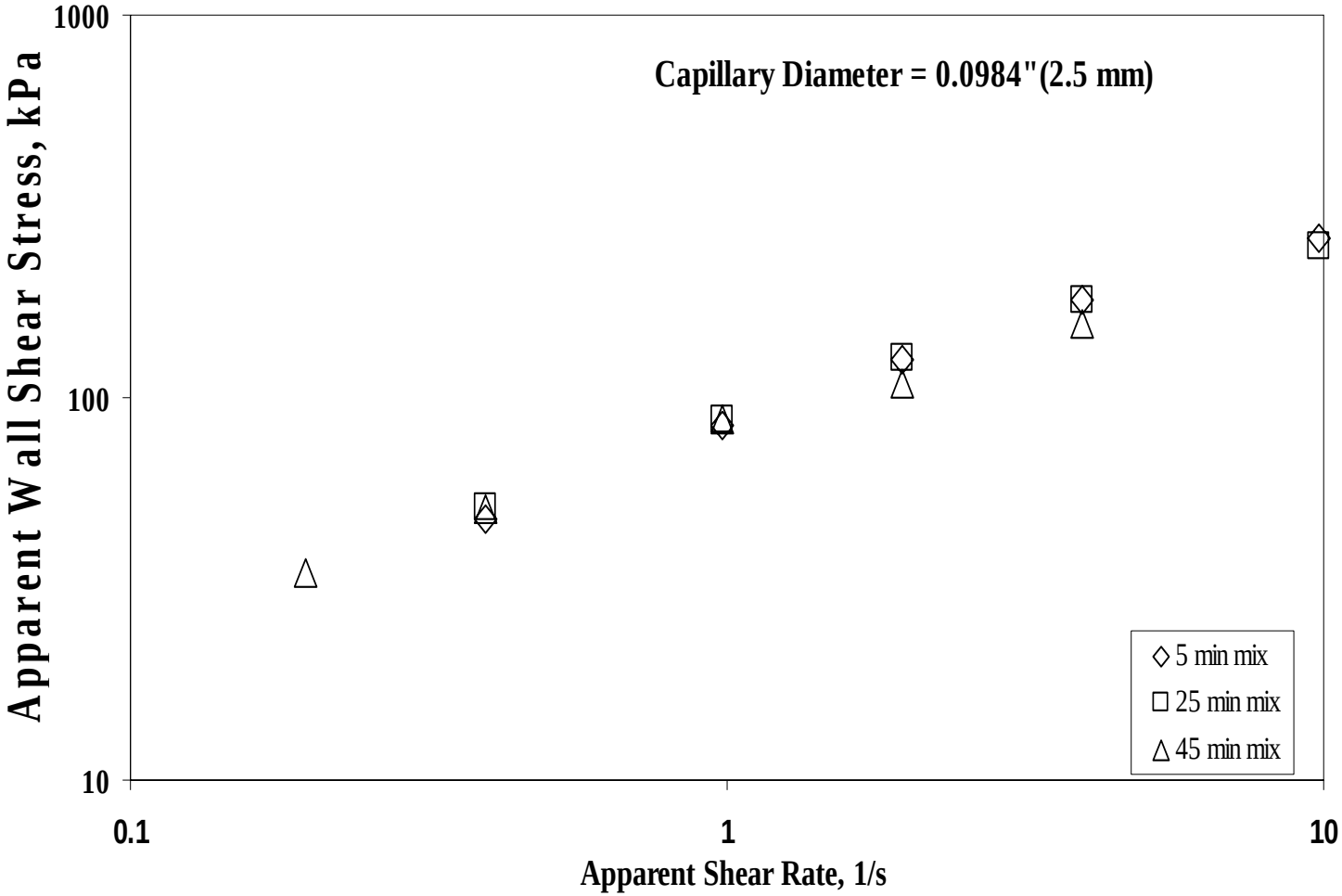
Magnitude of complex viscosity versus mixing index for amorphous (WXRD) at three frequencies



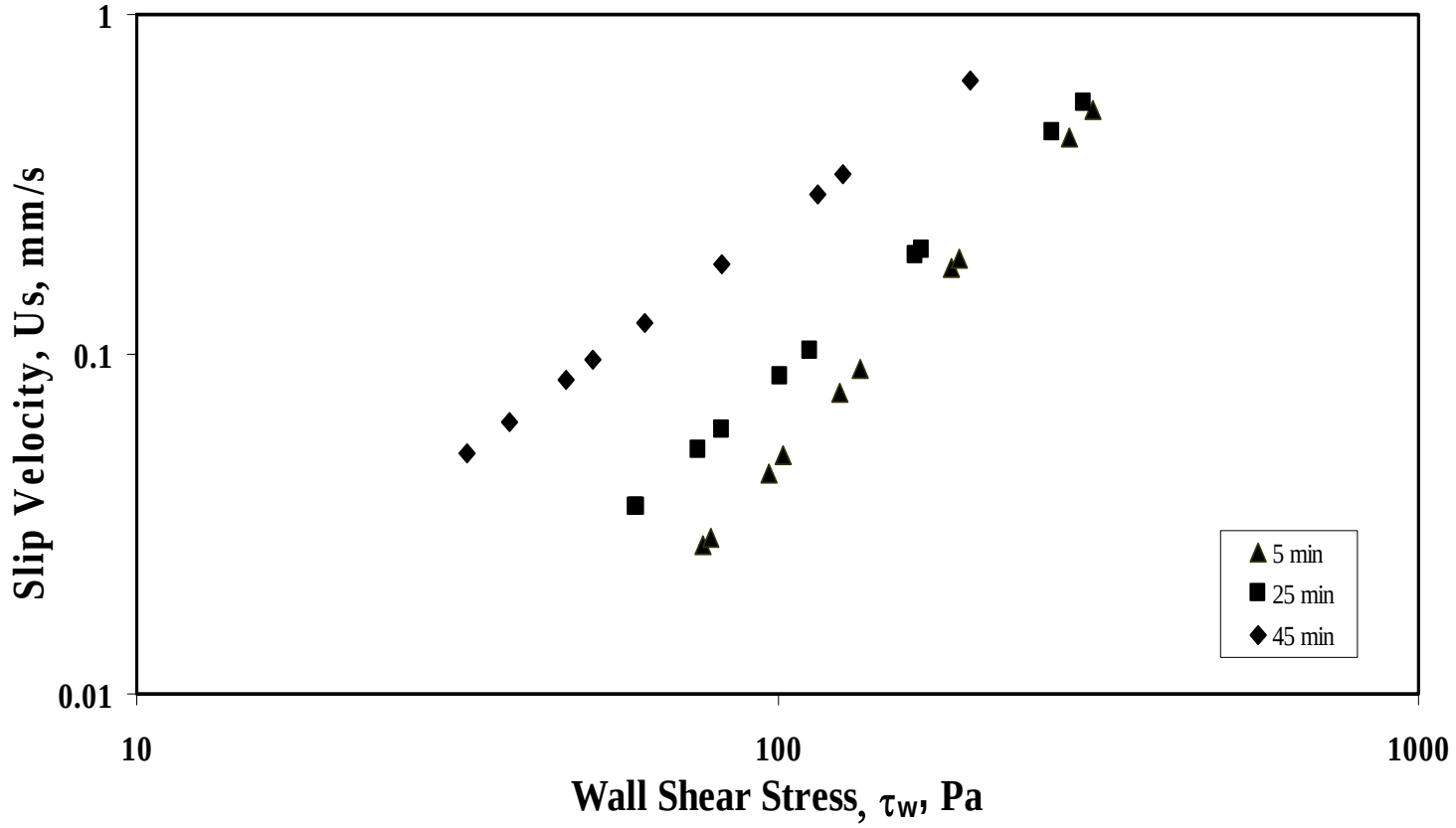
Magnitude of complex viscosity versus mixing index for graphite (WXRD) at three frequencies



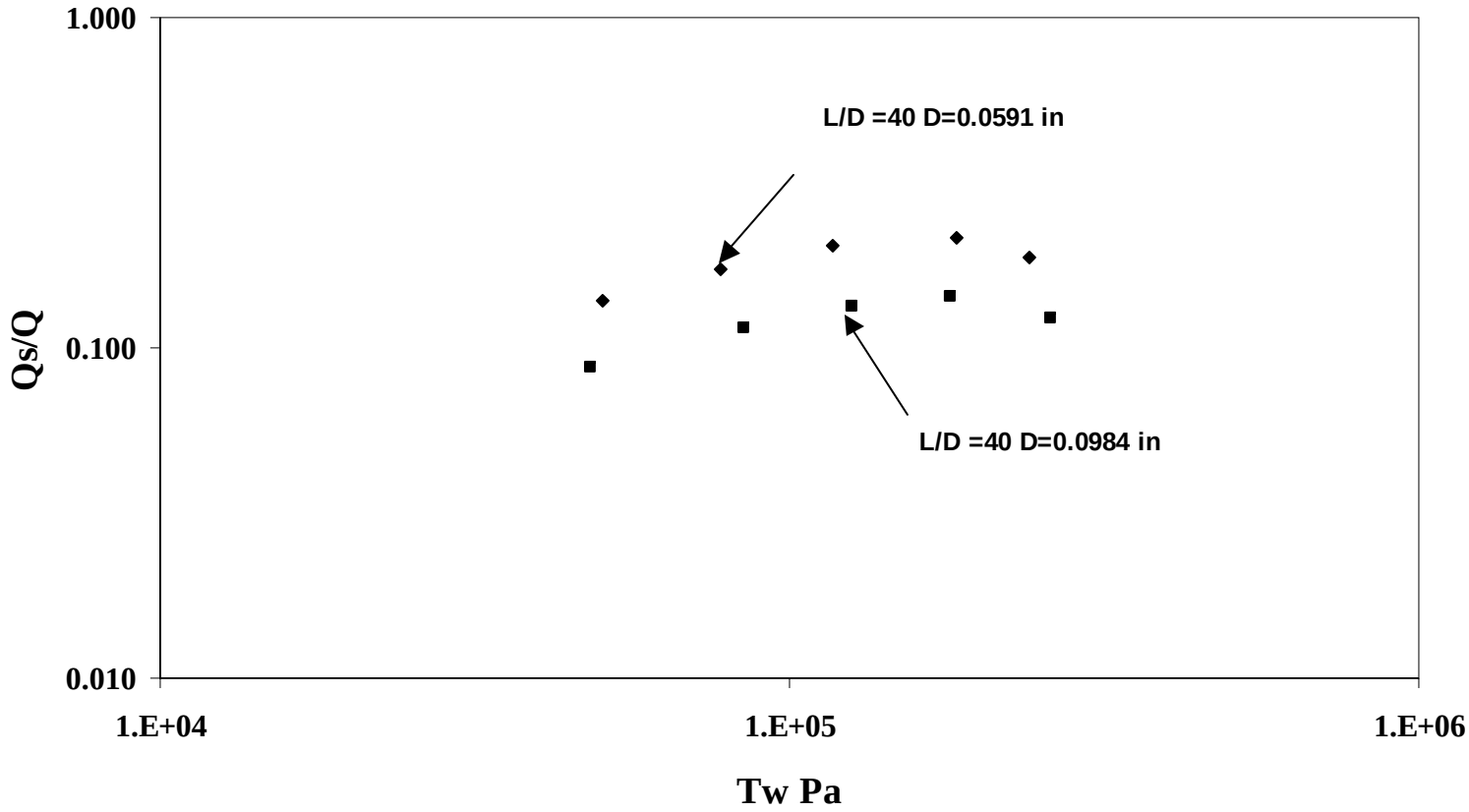
Apparent wall shear stress vs apparent shear rate for the batch mixed specimens



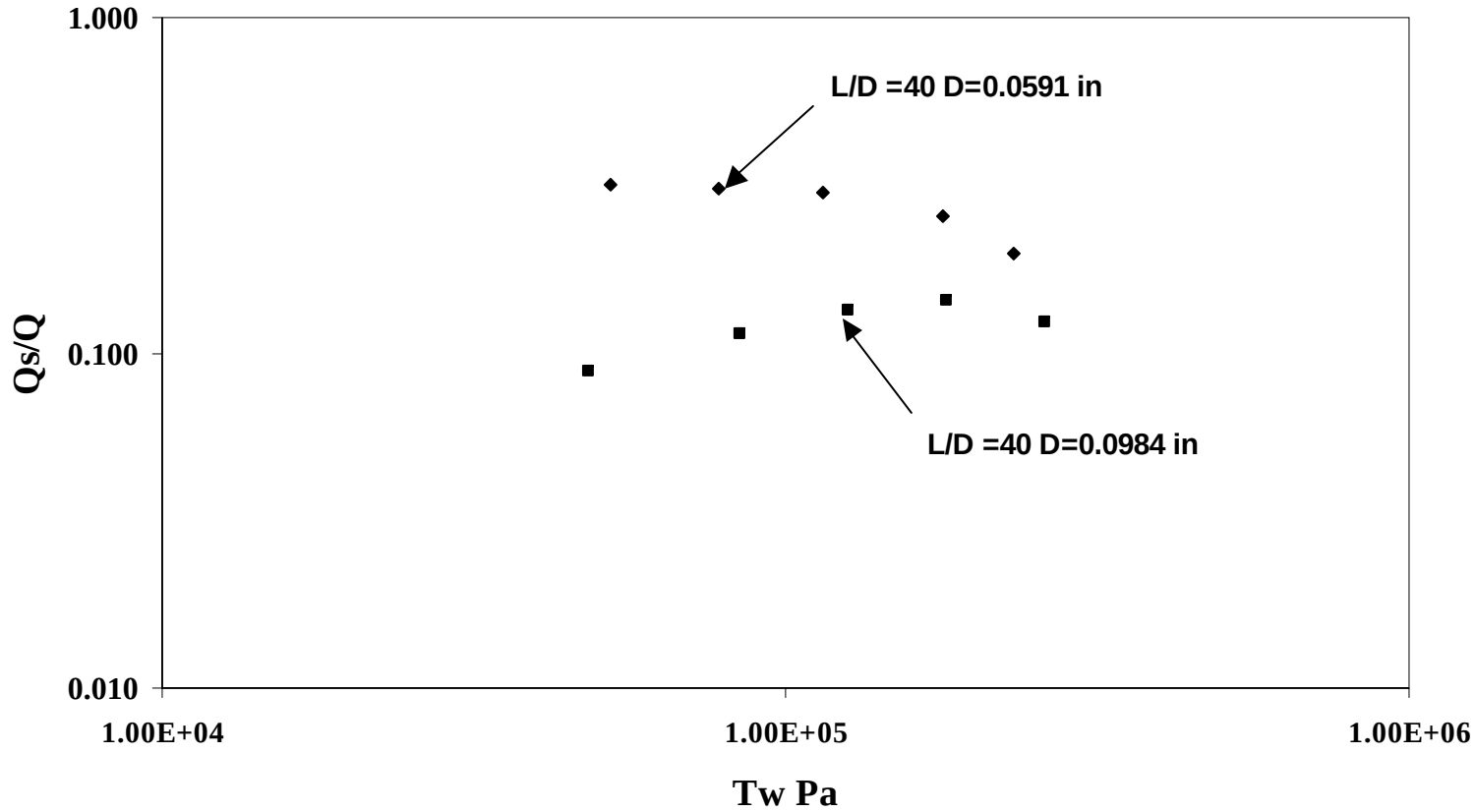
Apparent wall shear stress vs apparent shear rate for the batch mixed specimens



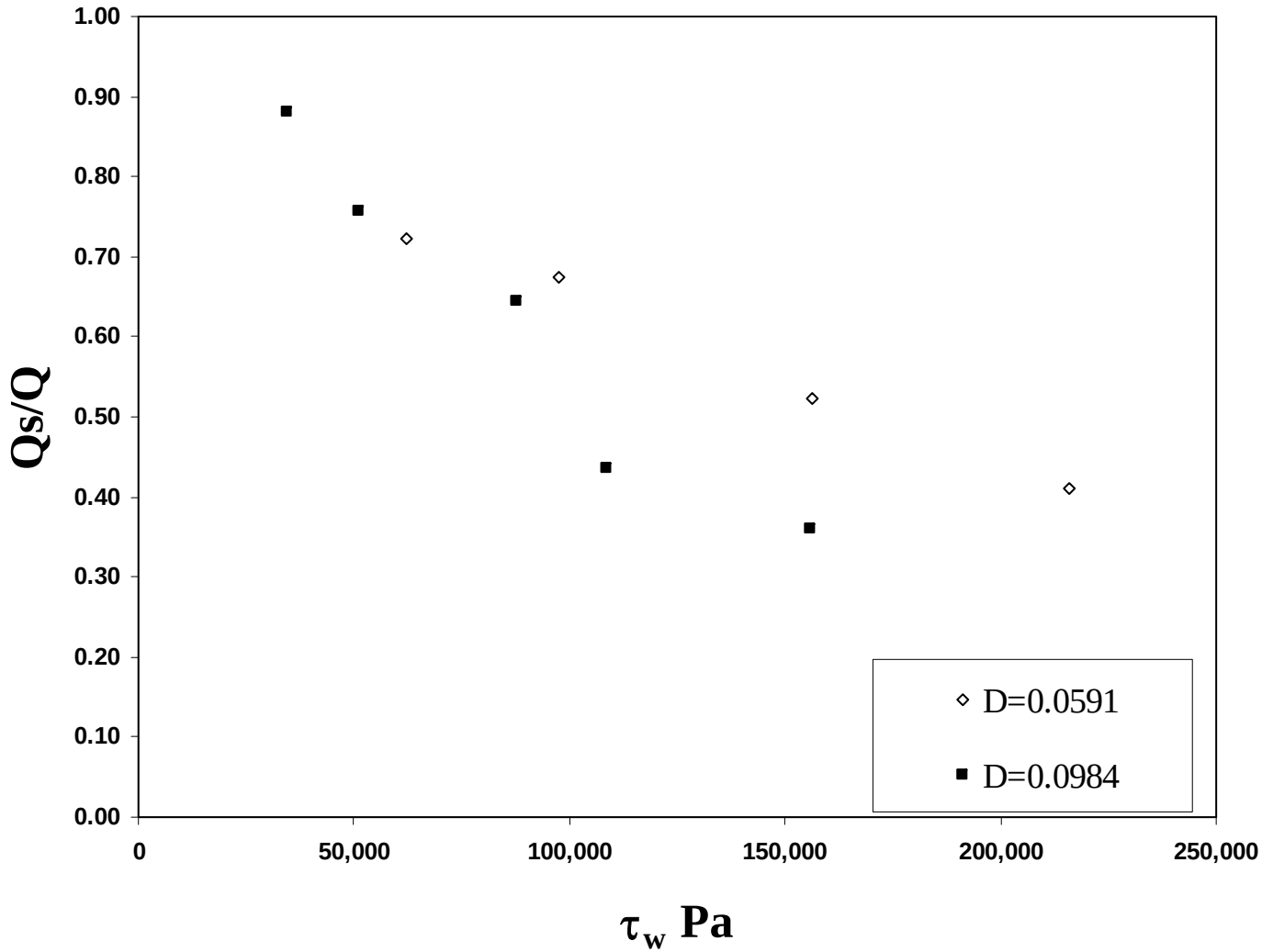
Comparison of slip velocities vs shear stress for the batch mixed specimens



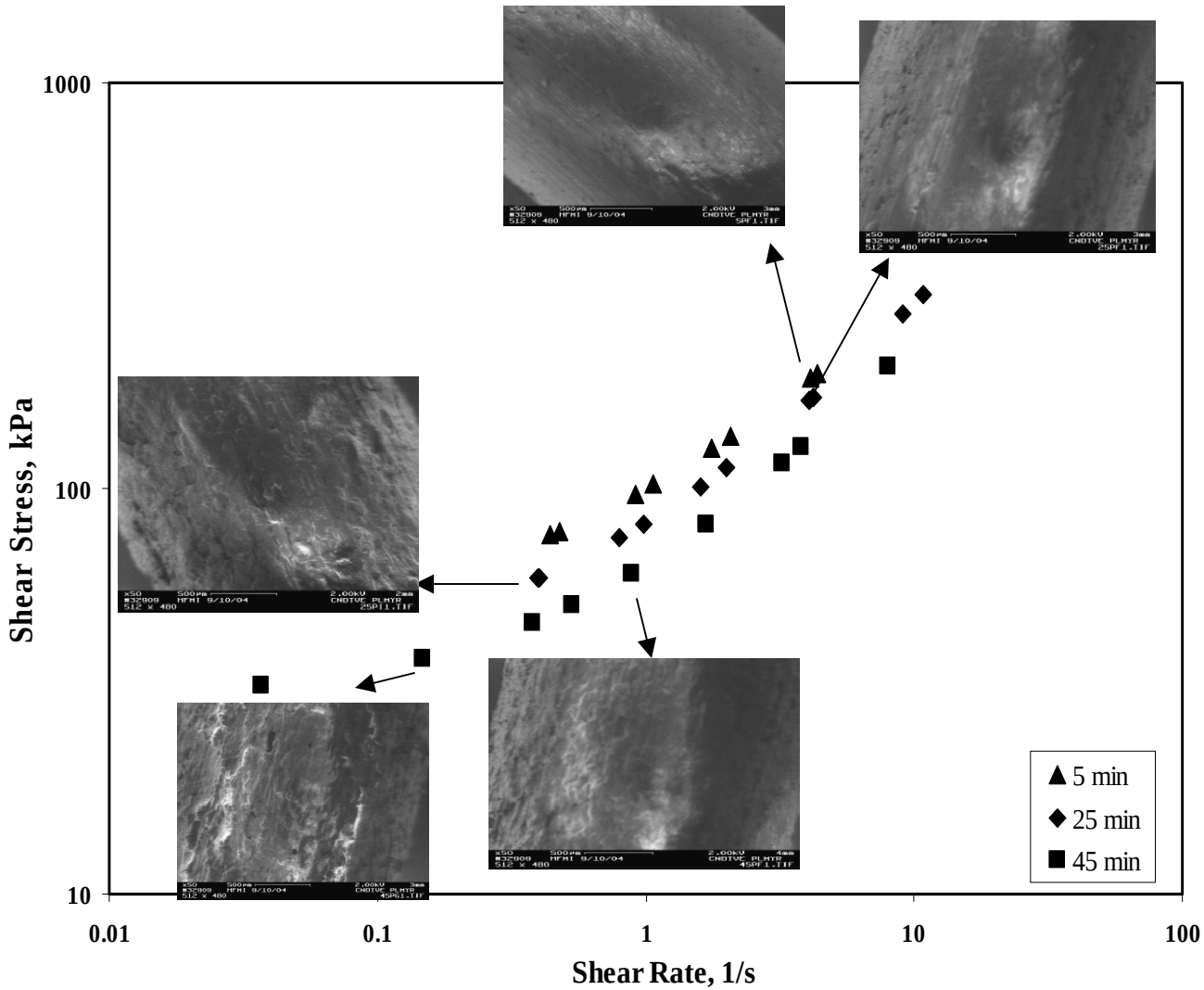
Qs/Q Vs. Tw for 5 min mixing at 95 ^{o}C.



Qs/Q Vs. Tw for 25 min mixing at 95 ^{o}C.

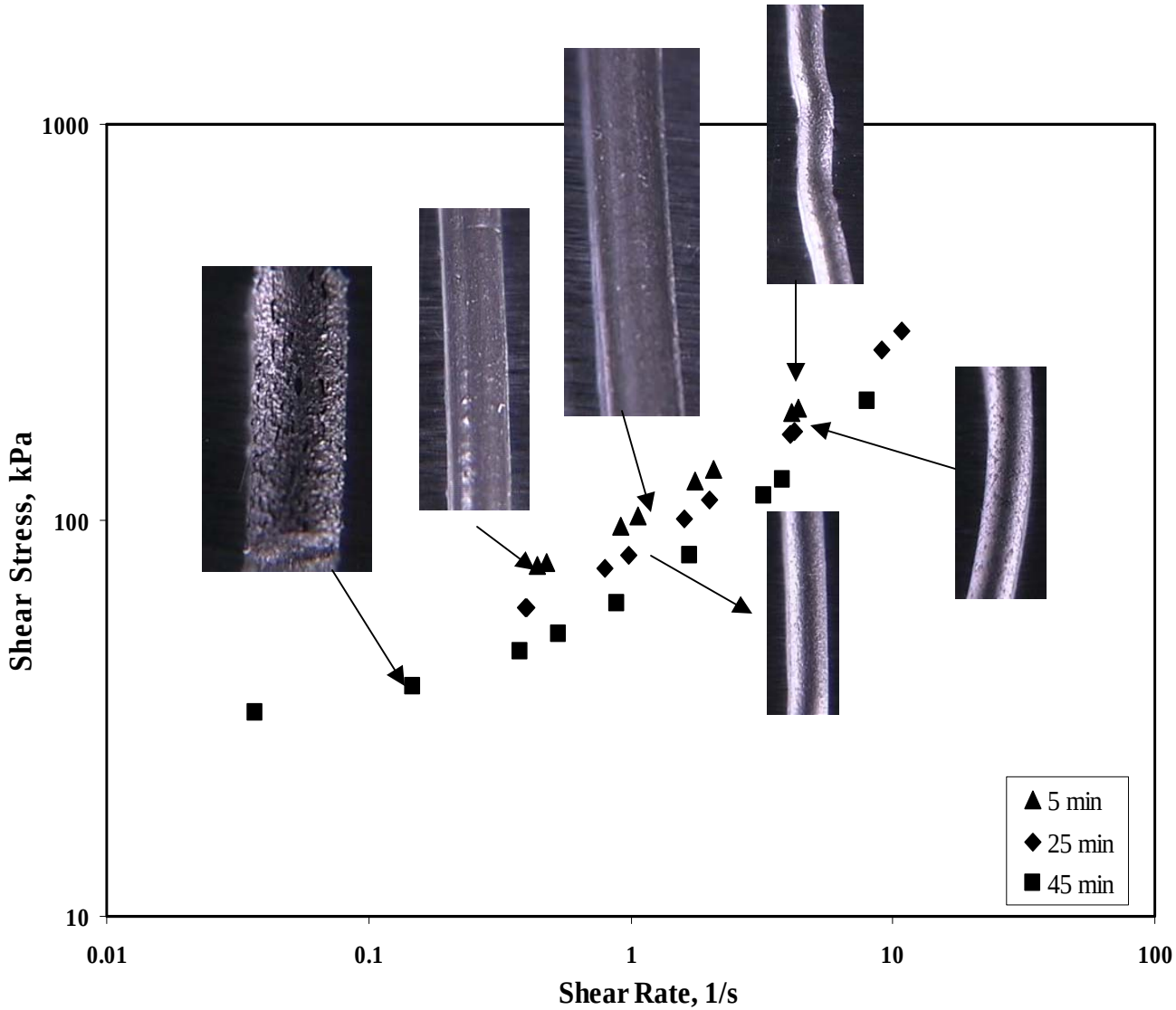


Qs/Q Vs. Tw for 45 min mixing at 95 ^{o}C.

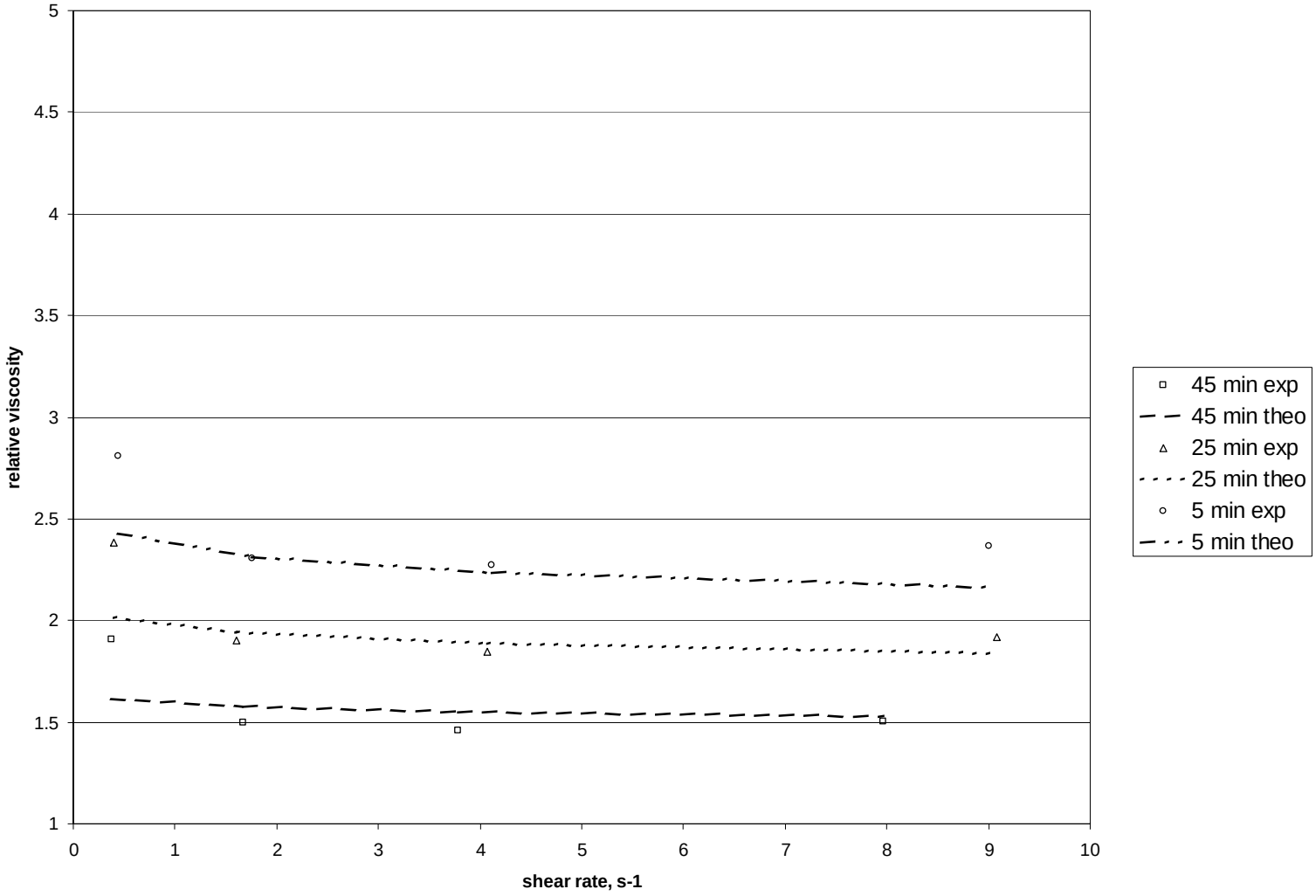


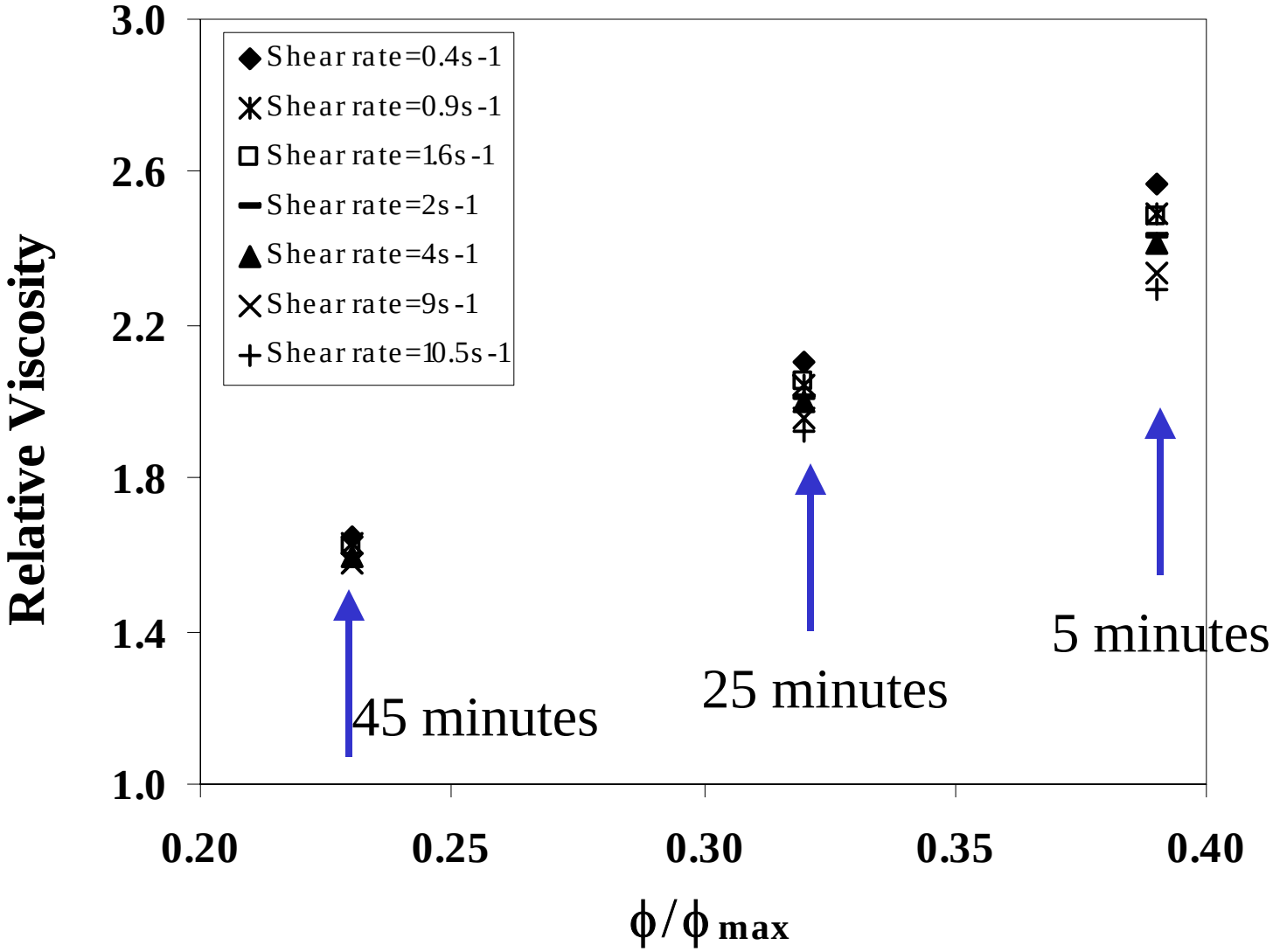
Comparison of shear stress vs shear rate for the batch mixed specimens

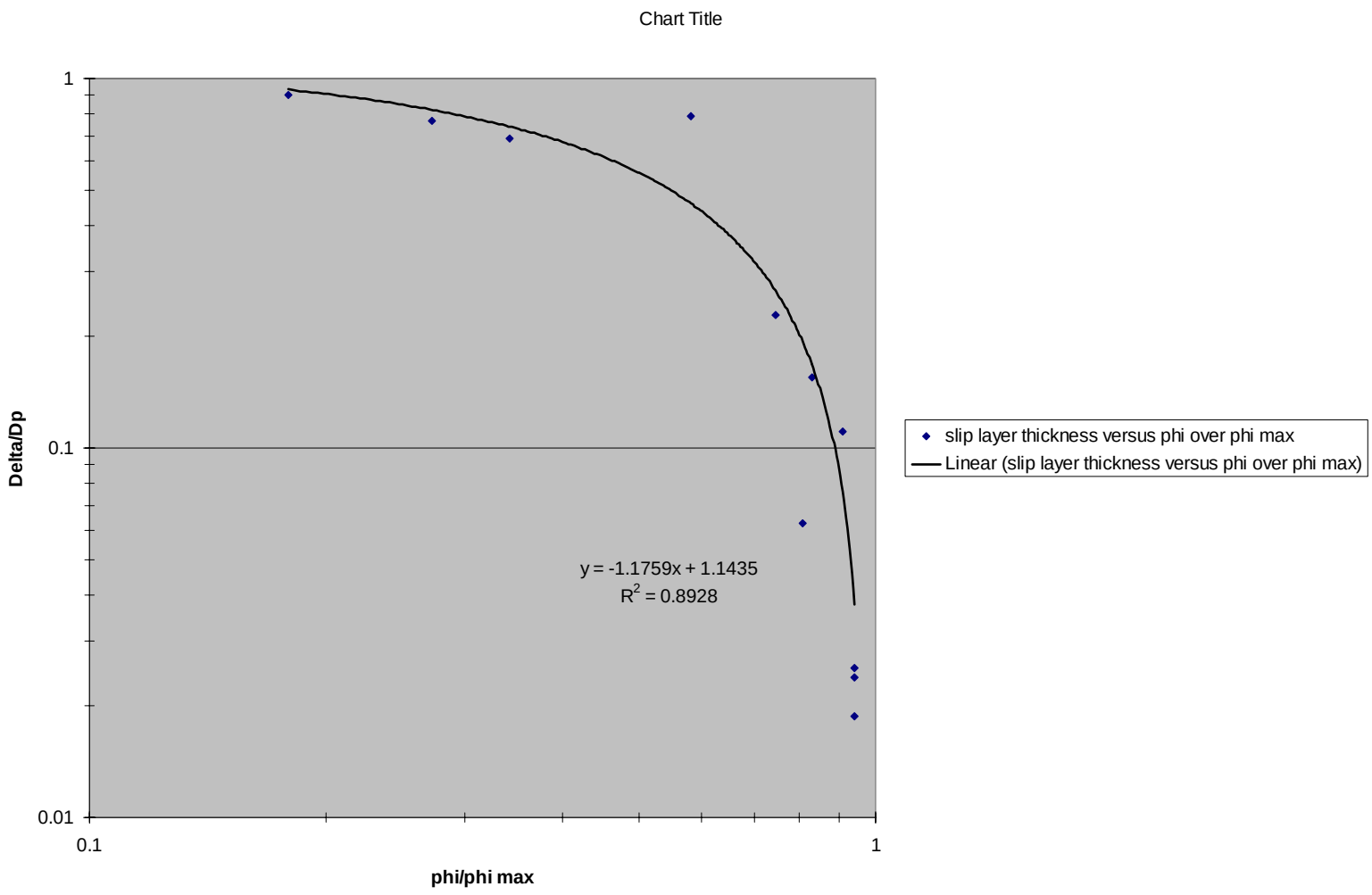
SEM micrographs



Comparison of shear stress vs shear rate for the batch mixed specimens, optical microscopy


5
4.5
4
3.5
3
2.5
2
1.5
1
relative viscosity
0
1
2
3
4
5
6
7
8
9
10
shear rate, s-1
45 min exp
45 min theo
25 min exp
25 min theo
5 min exp
5 min theo


Relative Viscosity
3.0
2.6
2.2
1.8
1.4
1.0
0.20
0.25
0.30
0.35
0.40
ϕ/ϕ max
Shear rate=0.4s-1
Shear rate=0.9s-1
Shear rate=1.6s-1
Shear rate=2s-1
Shear rate=4s-1
Shear rate=9s-1
Shear rate=10.5s-1
45 minutes
25 minutes
5 minutes



Plot the delta over Dp, hm versus phi over phi max

Conclusions

- Degree of mixing analysis using two different techniques (WAXD and TGA)
- Both methods agree for the conductive composite
- Degree of mixing affects the shear viscosity, elasticity and wall slip
- For one particular conductive suspension, increasing degree of mixing reduces the shear viscosity, elasticity and increases wall slip.