Nucleation Behavior of Polypropylene with a Nan-O-Sil Additive
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Samples and Request

- 3 Samples of Polypropylene
  - 1) Neat PP
  - 2) Nan-O-Sil Powder
  - 3) Nan-O-Sil Master Batch

  Request is to determine nucleation effect of added Nan-O-Sil on polypropylene specifically in nucleation geometry and effect on activation energy.

Experimental: Method

- Nucleation effect will be evaluated with isothermal differential scanning calorimetry.
- Sample is heated significantly higher than the equilibrium melting temperature and cooled rapidly to a temperature where crystallization occurs. Area under the curve is evaluated as fraction crystallized as a function of time. Experiment is repeated at temperatures so that 5 repetitions approximately 10 ^{o}C apart are obtained.

- Equation 1

$$X(t) = \frac{\int_{t_0}^{t_\infty} \left(\frac{dH_C}{dt} \right) dt}{\Delta H_C}$$

- Equation 1 describes the volume fraction crystallized as a function of time.

Experimental: Method

- The resultant curve represented by X(t) is evaluated using two mathematical models:
- 1) Avrami

$$X(t) = 1 - \exp(-k_a t^{n_a})$$

$$\log(-\ln(1 - X(t)) = \log k_a + n_a \log t$$

- Equation 2 and 3
- Equations 2 and 3 are the Avrami and linearized Avrami equations
- The Avrami parameter n is related to the nucleation geometry
  - n=1 – rod like growth, single dimension
  - n=2 – planar growth, two dimensions
  - n=3 – spherical growth, 3 dimensions
  - k = Avrami rate constant

Experimental: Method

- 2) Malkin Model

$$X(t) = 1 - \frac{C_0 + 1}{C_0 + \exp(C_1 t)})$$

- Equation 4 – Malkin Equation
- Malkin parameter C_0 is related to nucleation growth – it is the proportional to the ratio of secondary nucleation growth (propagation) to primary growth
- Malkin Parameter C_1 is a rate constant that is proportional to total nucleation.

Experimental: Method

- 3) Malkin relation to Avrami parameters k and n

$$X(t) = 1 - \frac{C_0 + 1}{C_0 + \exp(C_0 t)})$$

where

$$C_0 = 4n - 4$$

$$C_1 = \ln(4n - 2)\left(\frac{k}{\ln(2)}\right)^{1/n}$$

Experimental: Method

- Data calculated from Avrami parameters:

- Equation 5 $t_{1/2}$ $$t_{1/2} = \left(\frac{\ln 2}{k} \right)^{1/n}$$

- Equation 6 tau $$\tau = \frac{1}{t_{1/2}}$$

Experimental: Method

- 4) Calculation of Activation Energy – Effect of nucleation can be measured by comparing activation energy of non-nucleated samples to nucleated samples.
- The general equation used to calculate Activation energy is:

$$\Psi_{T_c} = \Psi_0 \exp(-\Delta E / RT)$$

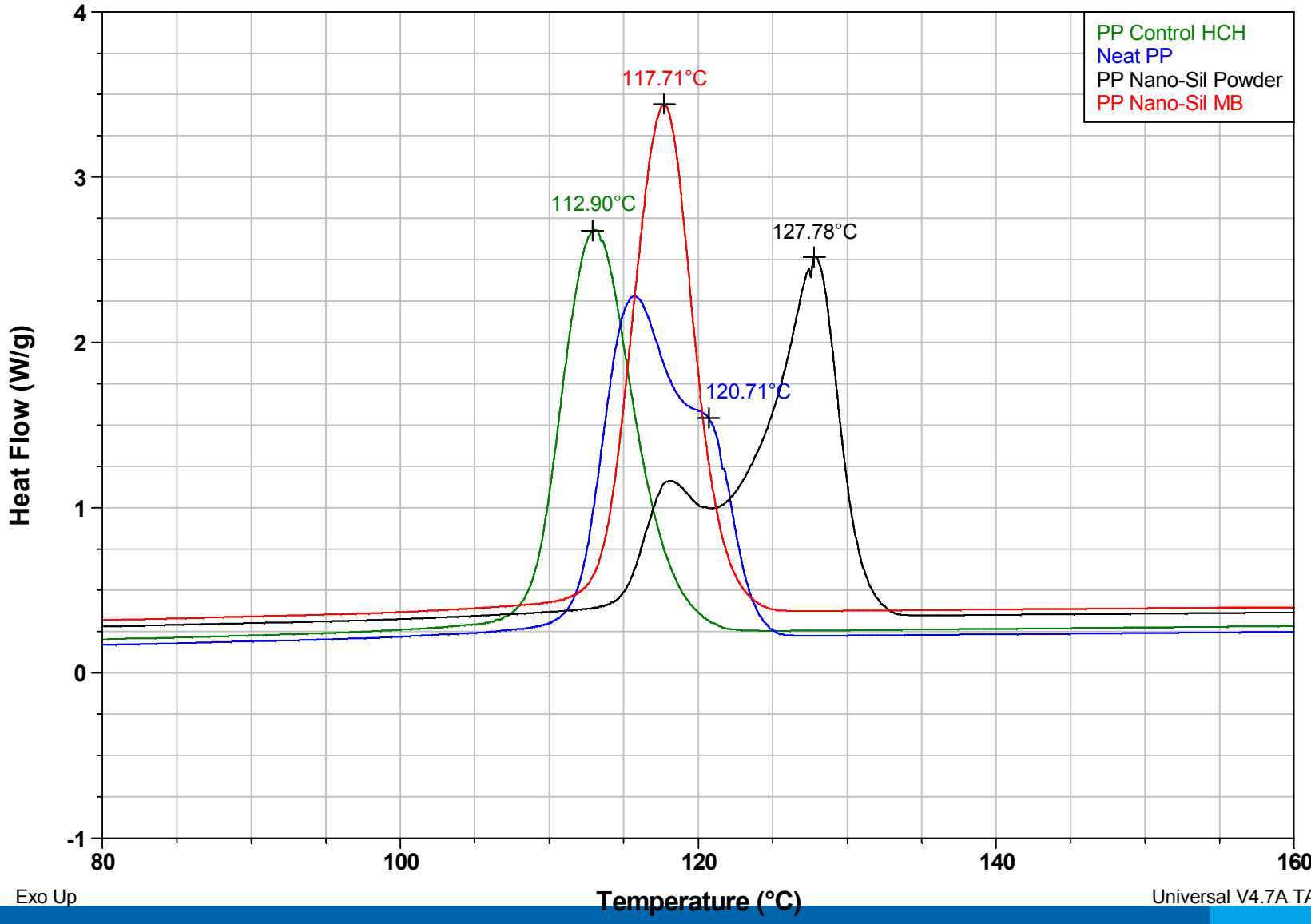
- **Equation 7**
- where Ψ can be
  - k
  - $k^{1/n}$
  - C_1
  - τ
  - $dX_{(t)}/ dt$

- ΔE = Crystallization Activation Energy
- T = Temperature (K)
- R = Gas Constant

Experimental: Method

- Polypropylene containing a nucleator will show some unique characteristics including:
  - Increased crystallization temperature upon dynamic cooling
  - Avrami geometric exponent (n) of around 2
  - Decreased Malkin C_0 constant – Malkin C_0 is directly proportional to the ratio of secondary nucleation to primary nucleation.
  - Lower crystallization activation energy
  - Higher rate constants, lower values of $t_{1/2}$ (higher τ)
  - Obvious differences in heat flow and fraction crystallized with respect to time

Experimental: Results – Survey Scans Cooling at 10 C / minute (Non-Isothermal)



Experimental: Results – Survey Scans Cooling at 10 C / minute (Non-Isothermal)

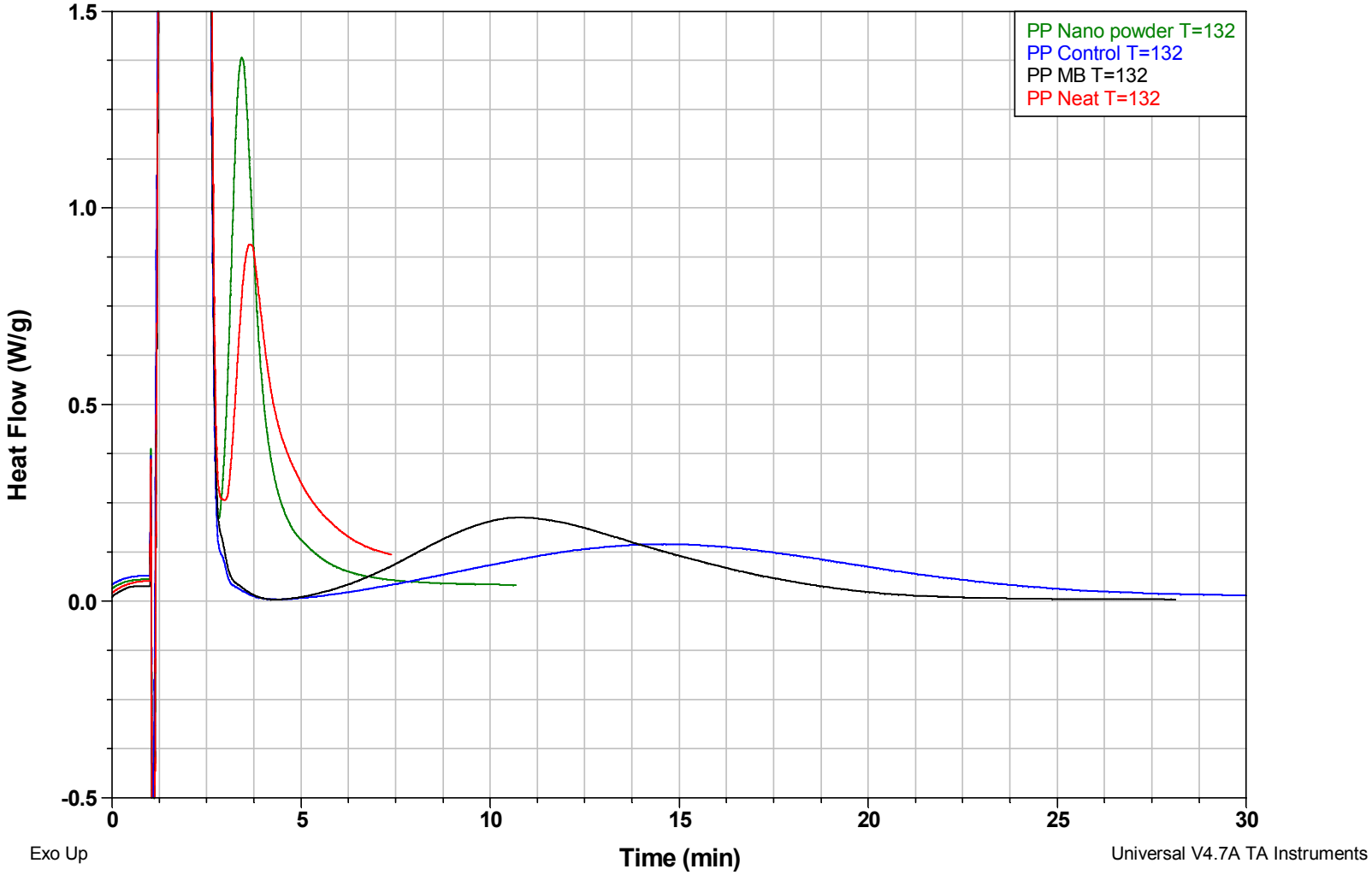
- Cooling scans show more than one crystallization peak in the neat PP and the Nano –Sil Powder. The PP Nano-sil master batch shows only one peak. The split peaks are indicative of poor dispersion of the nucleating agent.
- The neat PP appears to contain a nucleating agent†, so we will include a reference on non-nucleated polypropylene in the isothermal study.

†Polypropylene that has a significantly raised crystallization temperature is often times said to be 'nucleated'.

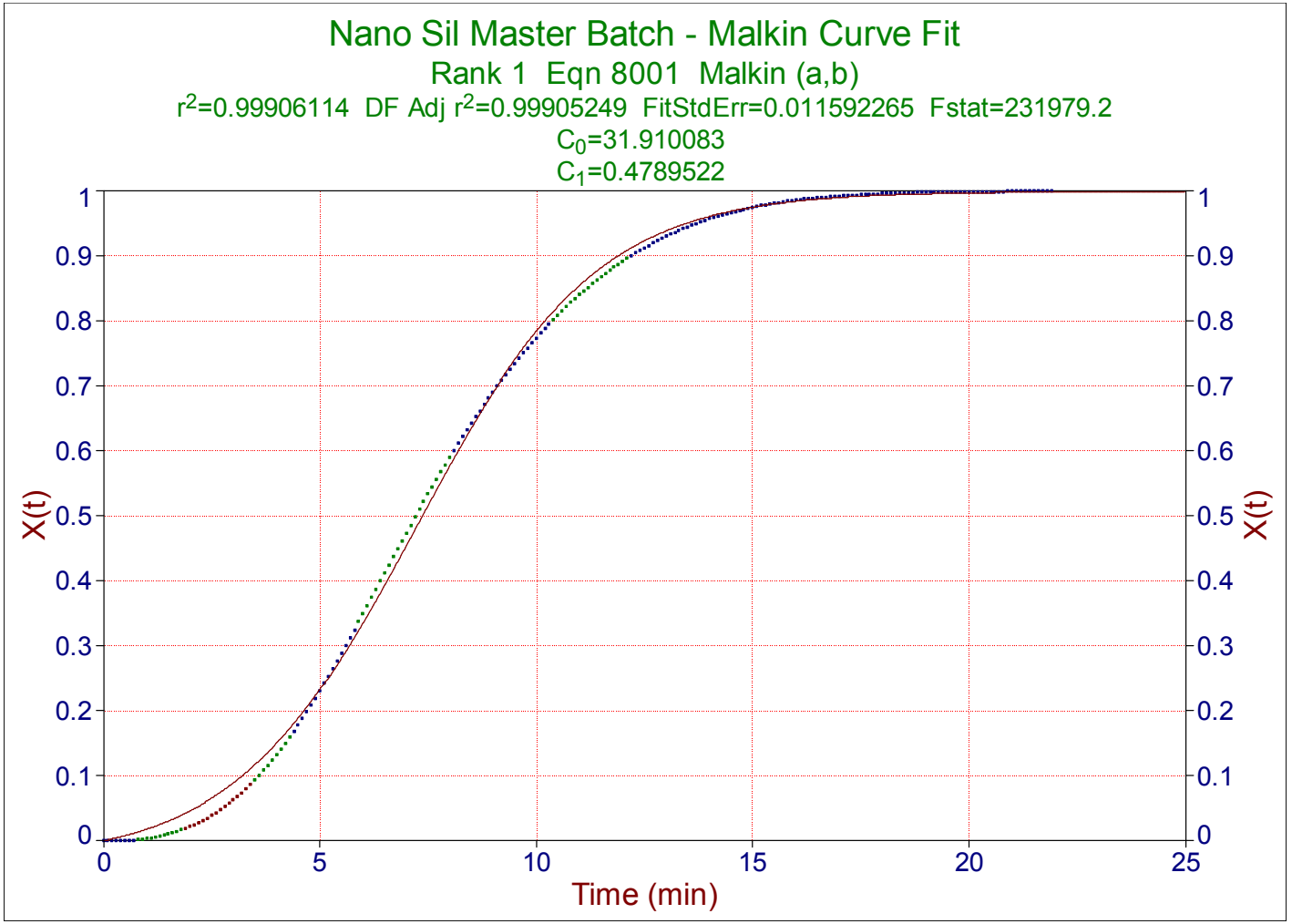
Experimental

- Isothermal Crystallization at 132 and 134 ^{o}C
- Data will be fit using the Malkin and Avrami models
- Activation energy will be determined by running the samples at 5 heating rates so that the temperature range is ~ 10 K apart.

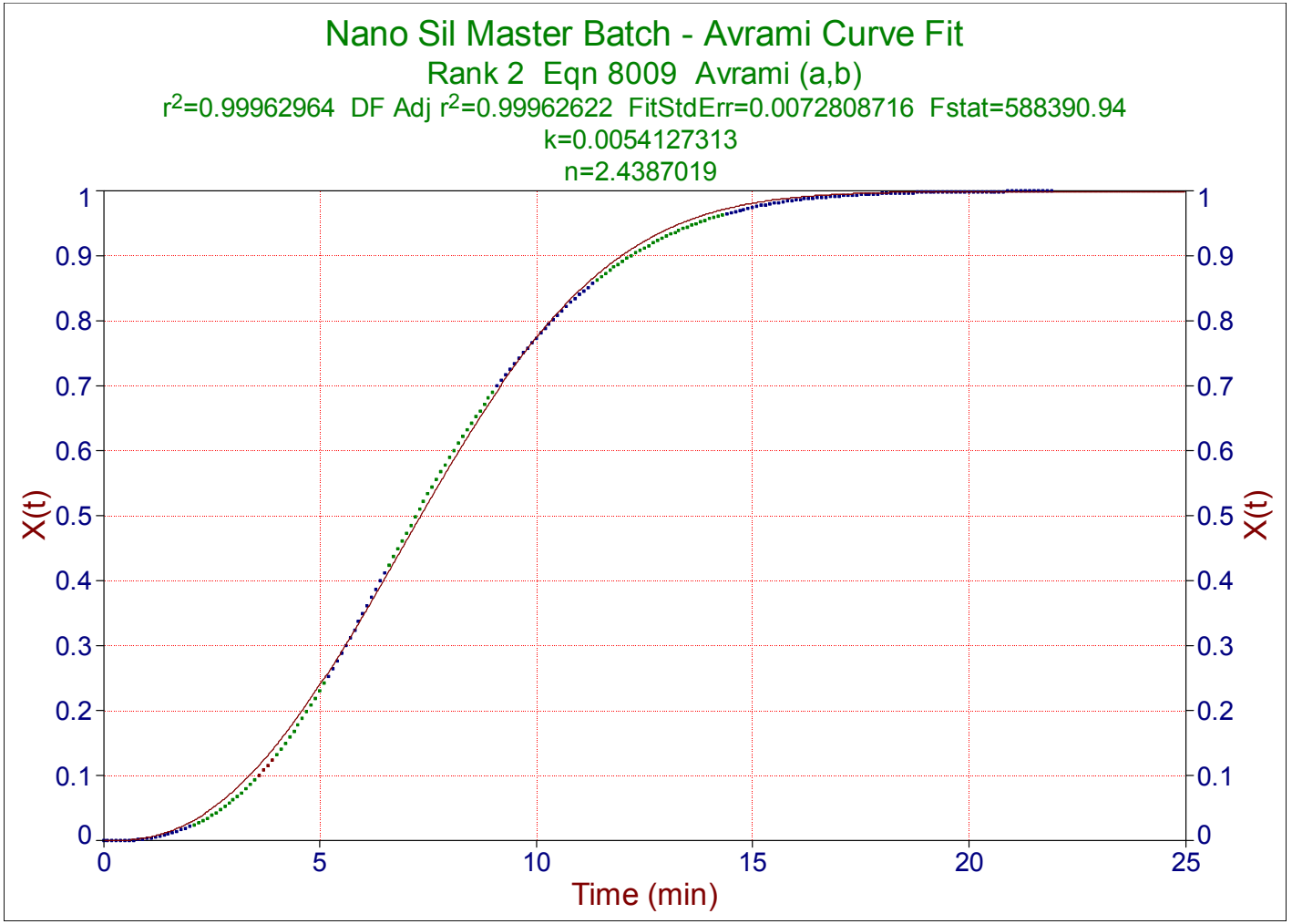
Comparison of Isotherms at 132 C



Example of Malkin Curve Fit



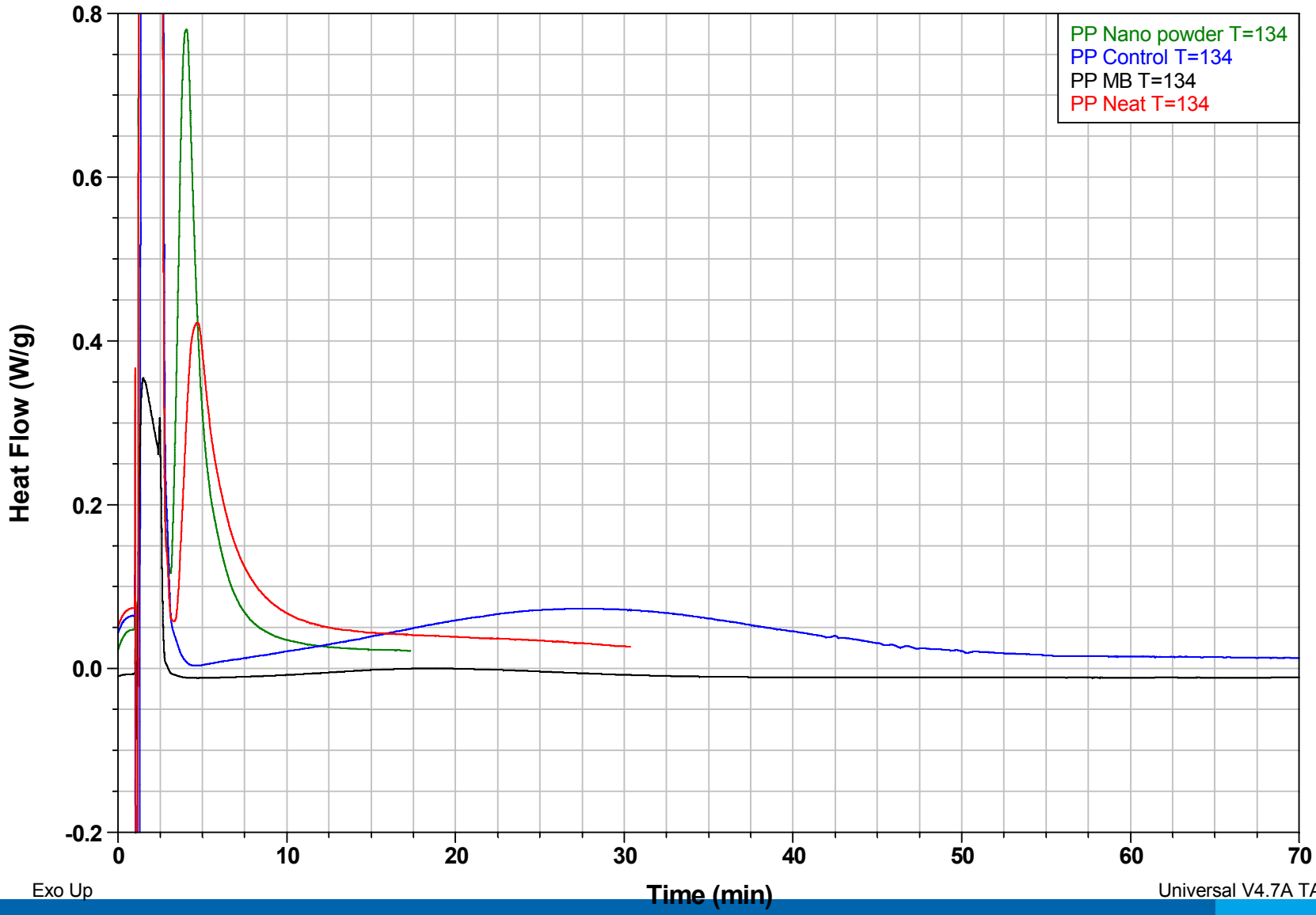
Example of Avrami Fit



Results: Isothermal Comparison at 132 C

Sample	Neat	Control	Master batch	Powder
ΔH (J/g)	43.51	99.71	99.55	54.85
$t_{1/2}$ from DSC	0.66	10.23	6.28	0.064
1/T (K-1)	0.00246889	0.0024689	0.0024689	0.0024689
Malkin Fit				
C0	7.359	35.867	31.910	23.732
C1	2.460	0.334	0.479	4.324
n	1.753	2.659	2.583	2.397
k	0.819	0.001	0.004	1.376
$t_{1/2}$ (min)	0.909	10.872	7.357	0.751
τ (s^{-1})	1.100	0.092	0.136	1.331
1/n ln(k)	-0.114	-2.524	-2.138	0.133
Avrami Fit				
n	1.736	2.511	2.439	2.259
k	0.837	0.002	0.005	1.346
$t_{1/2}$ (min)	0.897	10.813	7.314	0.745
τ (s^{-1})	1.114	0.092	0.137	1.342
1/n ln(k)	-0.103	-2.527	-2.140	0.132

Comparison of Isotherms at 134 C



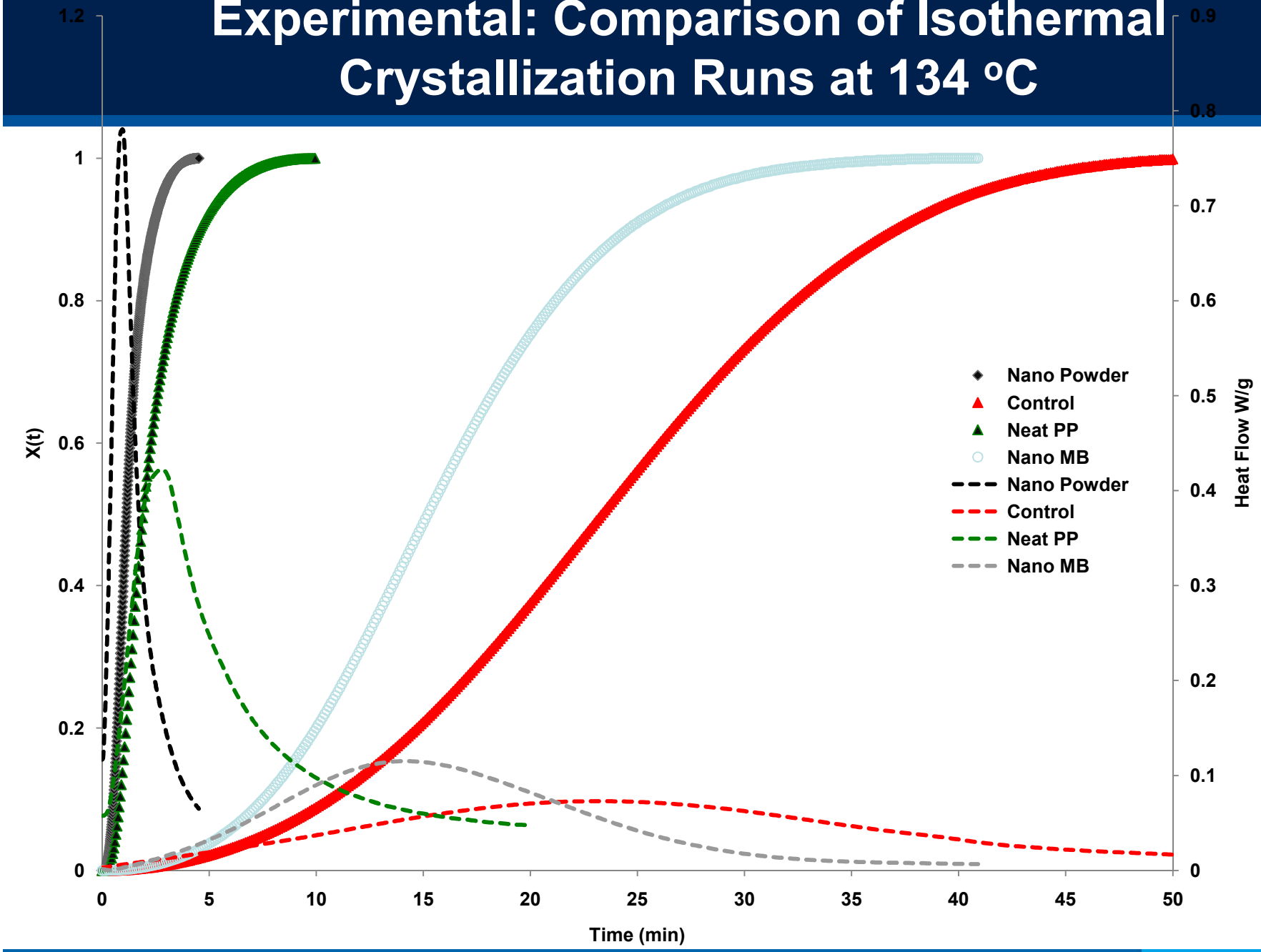
Results: Isothermal Comparison at 134 C

Sample	Neat	Control	Master batch	Powder
ΔH (J/g)	54.89	133.8	133.8	133.8
$t_{1/2}$ from DSC	1.38	103.2	111.5	55.78
1/T (K-1)	0.0024572	0.0024572	0.0024572	0.0024572
Malkin Fit				
C0	4.933	36.573	40.549	11.013
C1	0.942	0.157	0.244	2.149
n	1.580	2.671	2.739	1.954
k	0.222	0.000	0.000	0.490
$t_{1/2}$ (min)	2.055	23.309	15.366	1.194
τ (s^{-1})	0.487	0.043	0.065	0.837
1/n ln(k)	-0.952	-3.286	-2.866	-0.365
Avrami Fit				
n	1.593	2.537	2.578	1.896
k	0.225	0.000	0.001	0.506
$t_{1/2}$ (min)	2.028	23.187	15.297	1.180
τ (s^{-1})	0.493	0.043	0.065	0.847
1/n ln(k)	-0.937	-3.288	-2.870	-0.359

Results: Isothermal Crystallization

- Neat PP Sample
  - Appears to contain nucleating agent. This is evident from
    - Low Avrami exponent (n)
    - Low Malkin C_0
    - High rate constants (k and C_1) compared to the polypropylene control
    - Higher value of tau
    - Nucleator is poorly dispersed in this sample (split peaks in non-isothermal crystallization curve)
- Polypropylene Control – not nucleated, used for comparison in this work.
  - Typical Avrami ~3
  - Relatively high Malkin
  - Lower non-isothermal crystallization temperature
- Nan-O-Sil Powder
  - Sample is nucleated.
    - Low Avrami exponent (n)
    - Low Malkin C_0
    - High rate constants (k and C_1) compared to the polypropylene control
    - Higher value of tau
    - Nucleator is also poorly dispersed in this sample (split peaks in non-isothermal crystallization curve)
- Nan-O-Sil Master batch
  - Sample crystallizes significantly slower than either the Nan-O-Sil powder or the neat polypropylene sample.
  - Has similar characteristics as the polypropylene control.

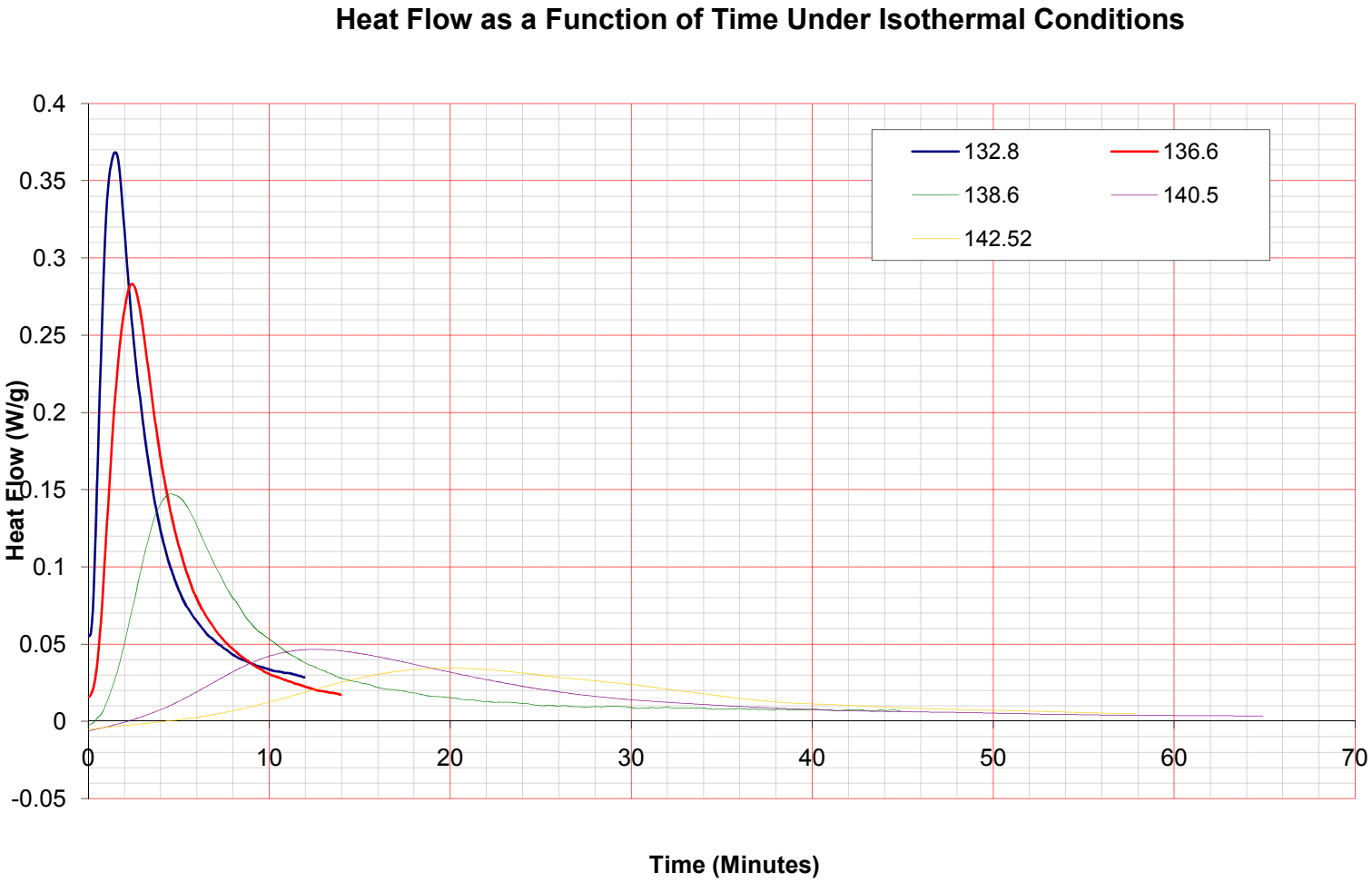
Experimental: Comparison of Isothermal Crystallization Runs at 134 °C



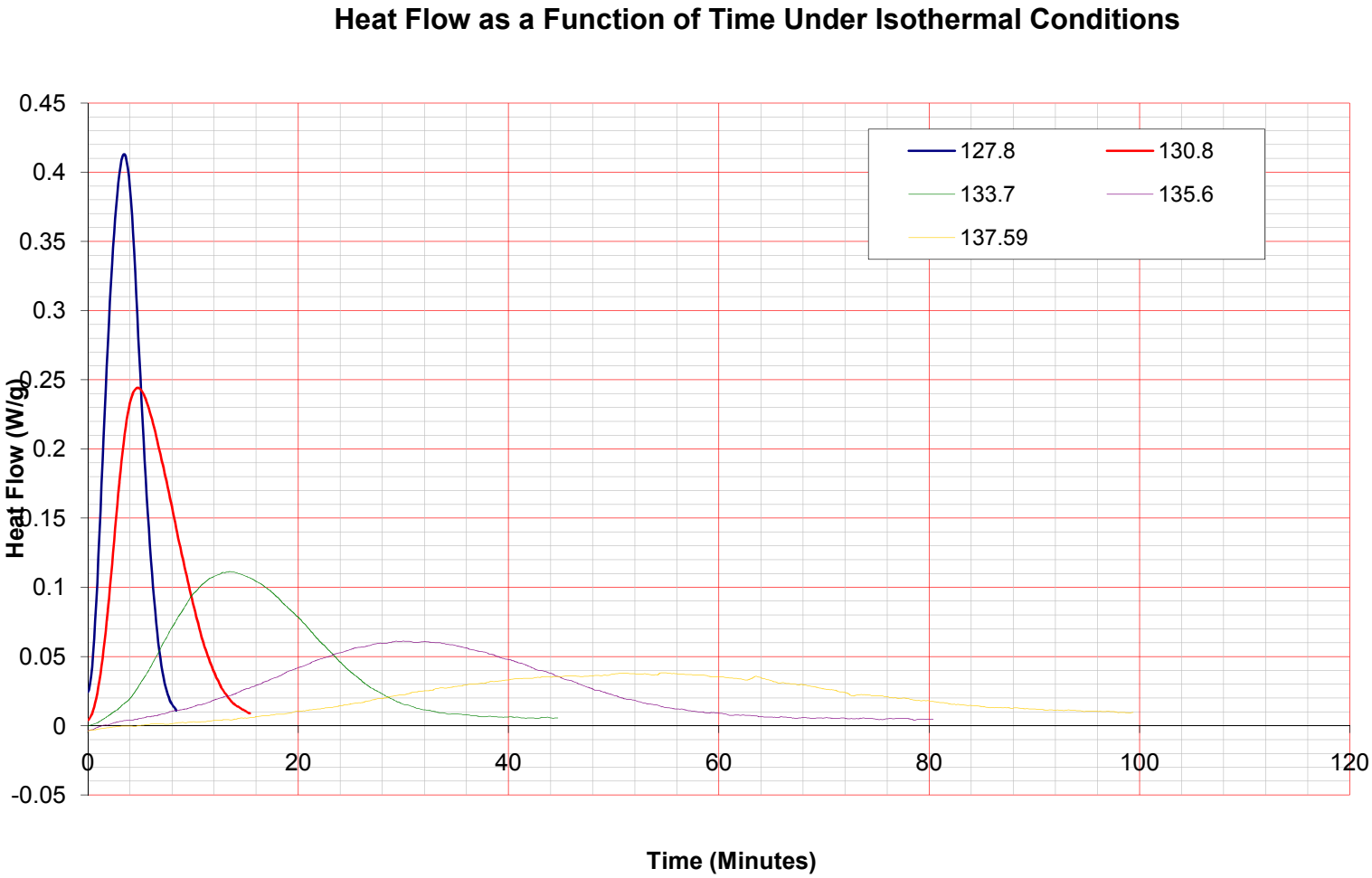
Experimental: Isothermal Crystallization Runs to Determine ΔE (Activation Energy)

- Isothermal crystallization experiments are carried out at 4-5 different temperatures that span about 10 K if possible. This ensures that the calculation of ΔE is from a reasonably linear area of the functions described in Equation 7.
- For calculations of ΔE, $\psi = 1/n \ln k$.
- For the isoconversional method, $\psi = dX(t) / dt$

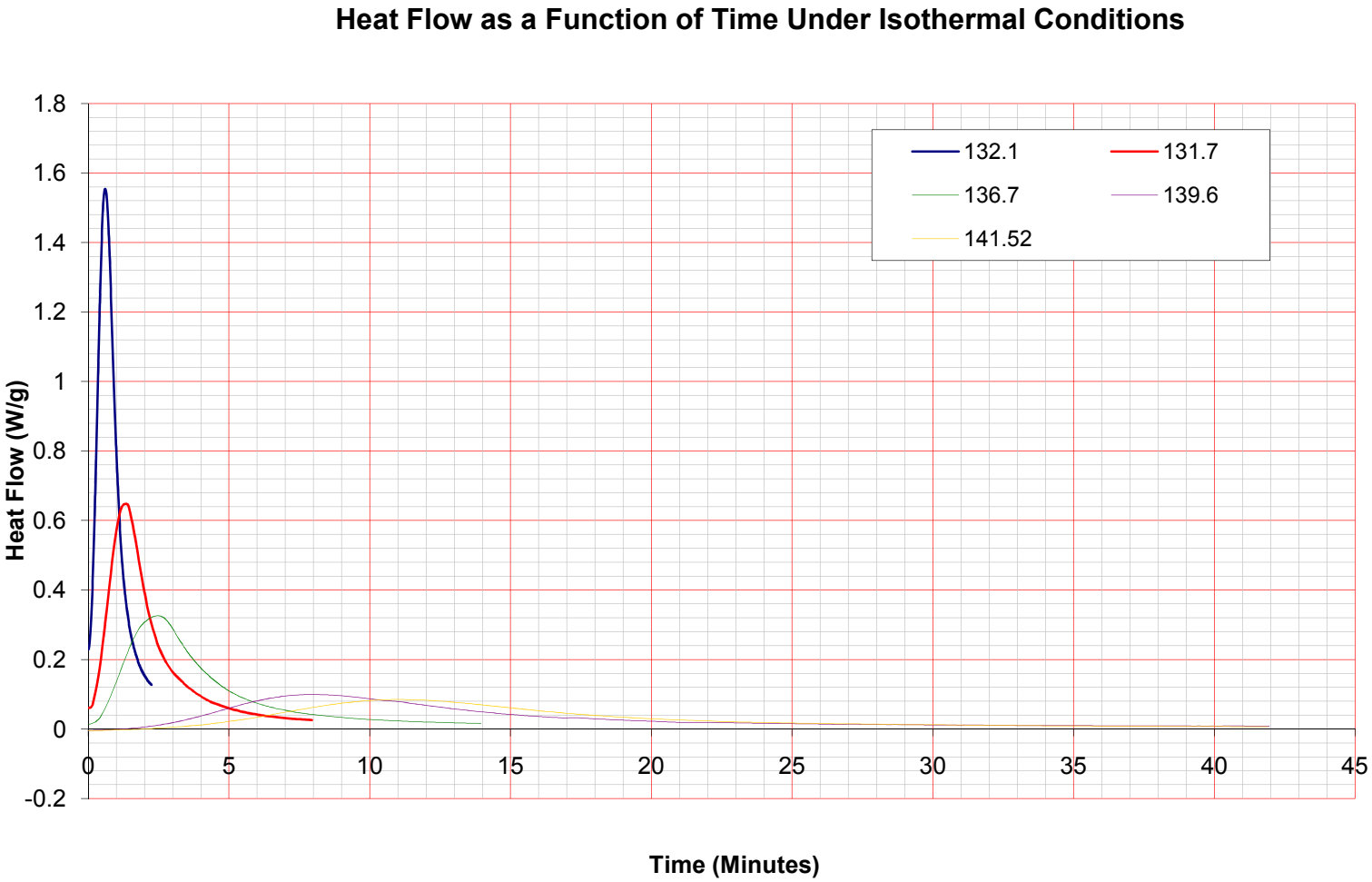
Experimental: Results Isothermal Crystallization – Neat PP



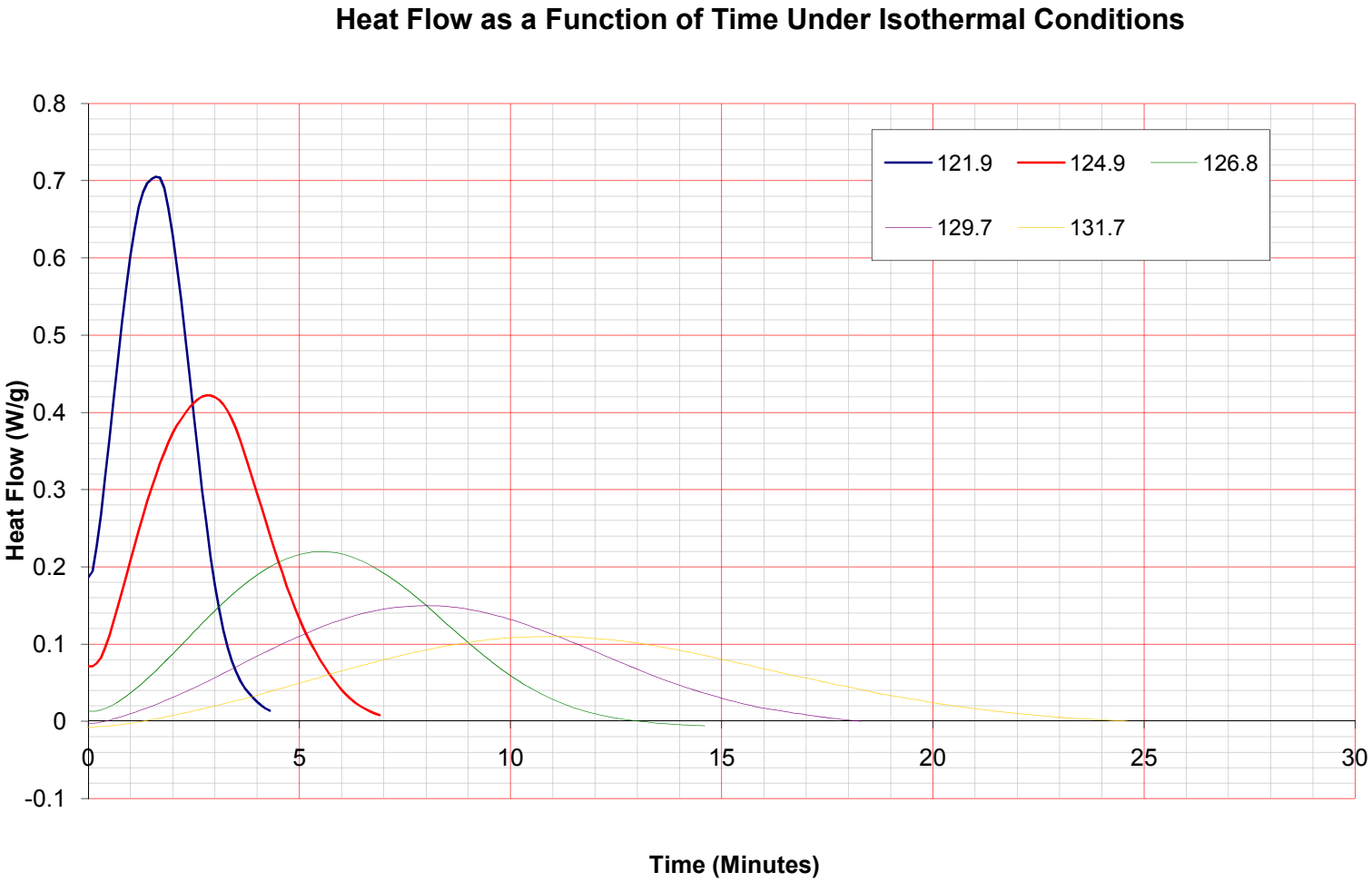
Experimental: Results Isothermal Crystallization – Nan-O-Sil Master Batch



Experimental: Results Isothermal Crystallization – Nan-O-Sil Powder



Experimental: Results Isothermal Crystallization – Polypropylene Control



Results: Kinetic Data for Neat PP Sample

T ° C	132.8	136.6	138.6	140.5	142.52
ΔH (J/g)	50.42	62.03	75.7	66.46	52.99
$t_{1/2}$ from DSC	1.5	2.43	4.57	12.4	19.11
1/T (K-1)	0.00246366	0.0024403	0.002429	0.0024173	0.002405755
Malkin Fit					
C0	7.101	8.134	2.206	8.004	29.320
C1	1.029	0.690	0.190	0.127	0.151
n	1.736	1.800	1.317	1.793	2.529
k	0.184	0.078	0.048	0.004	0.000
$t_{1/2}$ (min)	2.146	3.355	7.566	18.093	22.852
τ (s^{-1})	0.466	0.298	0.132	0.055	0.044
1/n ln(k)	-0.975	-1.414	-2.302	-3.100	-3.274
Avrami Fit					
n	1.727	1.771	1.366	1.770	2.389
k	0.190	0.083	0.044	0.004	0.000
$t_{1/2}$ (min)	2.118	3.313	7.499	17.859	22.710
τ (s^{-1})	0.472	0.302	0.133	0.056	0.044
1/n ln(k)	-0.962	-1.405	-2.283	-3.090	-3.276

Results: Kinetic Data for Nan-O-Sil Master Batch

T ° C	127.8	130.8	133.7	135.6	137.59
ΔH (J/g)	89.6	96.41	108.4	118.3	103.5
$t_{1/2}$ from DSC	3.46	4.7	13.5	29.3	51.14
1/T (K-1)	0.00249401	0.0024759	0.002458	0.0024464	0.00243463
Malkin Fit					
C0	46.337	27.891	38.739	49.971	66.269
C1	1.107	0.578	0.243	0.126	0.086
n	2.827	2.498	2.709	2.877	3.067
k	0.020	0.008	0.000	0.000	0.000
$t_{1/2}$ (min)	3.503	5.882	15.243	31.297	49.137
τ (s^{-1})	0.285	0.170	0.066	0.032	0.020
1/n ln(k)	-1.383	-1.919	-2.859	-3.571	-4.014
Avrami Fit					
n	2.663	2.368	2.549	2.708	2.896
k	0.025	0.011	0.001	0.000	0.000
$t_{1/2}$ (min)	3.489	5.838	15.174	31.188	49.048
τ (s^{-1})	0.287	0.171	0.066	0.032	0.020
1/n ln(k)	-1.387	-1.919	-2.863	-3.575	-4.019

Results: Kinetic Data for Nan-O-Sil Powder

T ° C	132.1	131.7	136.7	139.6	141.52
ΔH (J/g)	59.22	63.01	66.85	71.5	68.98
$t_{1/2}$ from DSC	0.61	1.36	2.46	7.85	11.05
1/T (K-1)	0.00246792	0.0024701	0.0024402	0.002423	0.002411556
Malkin Fit					
C0	30.749	13.185	9.265	10.743	23.989
C1	5.037	1.650	0.765	0.229	0.241
n	2.559	2.052	1.865	1.941	2.403
k	1.774	0.249	0.081	0.006	0.001
$t_{1/2}$ (min)	0.693	1.648	3.164	11.097	13.497
τ (s^{-1})	1.444	0.607	0.316	0.090	0.074
1/n ln(k)	0.224	-0.678	-1.348	-2.596	-2.755
Avrami Fit					
n	2.406	1.968	1.819	1.881	2.258
k	1.702	0.265	0.087	0.008	0.002
$t_{1/2}$ (min)	0.688	1.631	3.125	10.971	13.402
τ (s^{-1})	1.453	0.613	0.320	0.091	0.075
1/n ln(k)	0.221	-0.675	-1.341	-2.590	-2.758

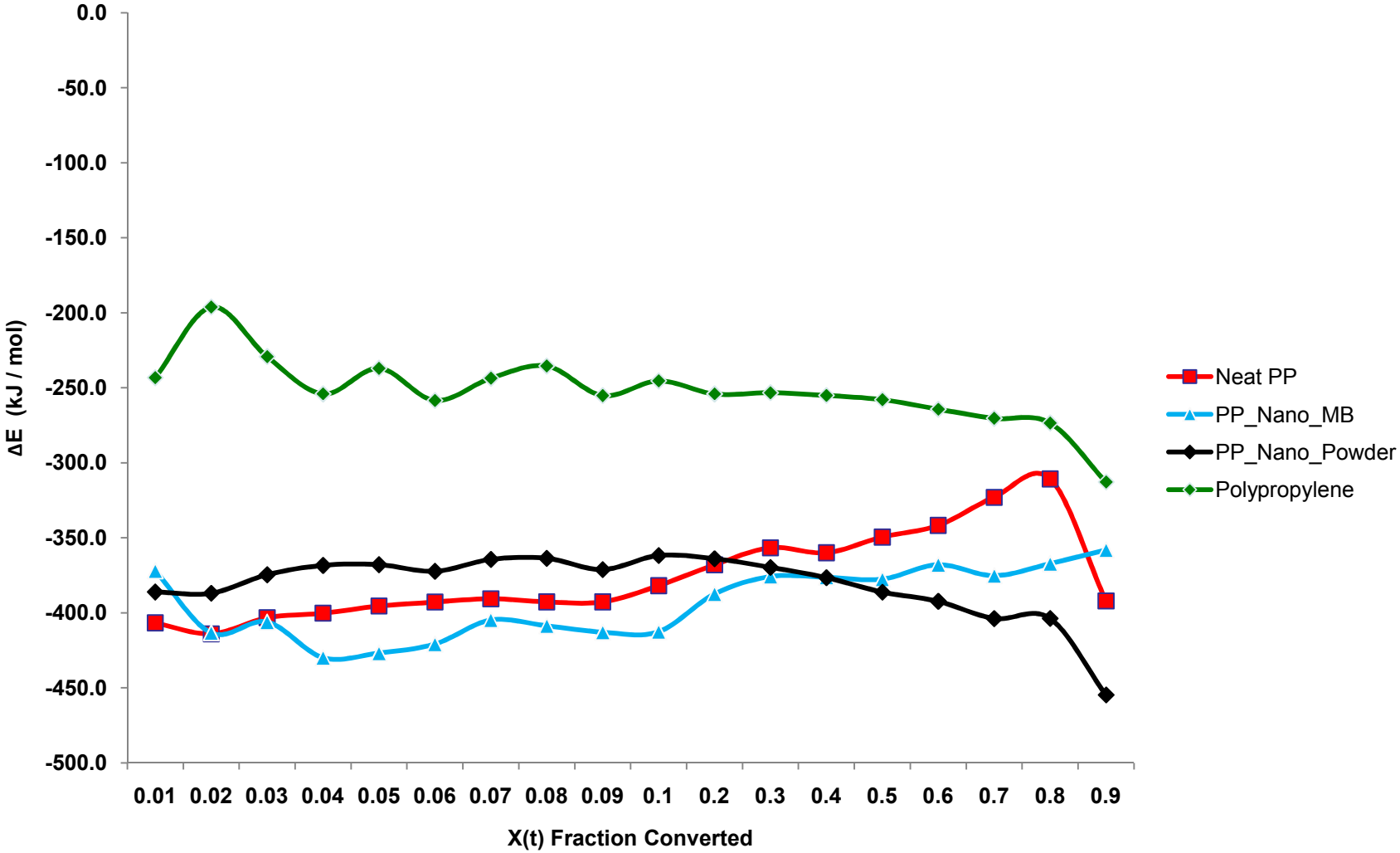
Results: Kinetic Data for PP Control

T ° C	121.9	124.9	126.8	129.7	131.7
ΔH (J/g)	66.09	74.15	82.7	83.5	83.49
$t_{1/2}$ from DSC	1.69	2.89	5.56	8.01	11.16
1/T (K-1)	0.00253139	0.0025125	0.0025003	0.0024823	0.002470051
Malkin Fit					
C0	38.756	39.867	42.438	42.260	46.352
C1	2.271	1.286	0.652	0.456	0.344
n	2.709	2.728	2.769	2.766	2.827
k	0.184	0.038	0.005	0.002	0.001
$t_{1/2}$ (min)	1.633	2.904	5.818	8.313	11.262
τ (s^{-1})	0.612	0.344	0.172	0.120	0.089
1/n ln(k)	-0.626	-1.201	-1.893	-2.250	-2.551
Avrami Fit					
n	2.567	2.579	2.613	2.601	2.669
k	0.194	0.045	0.007	0.003	0.001
$t_{1/2}$ (min)	1.642	2.892	5.793	8.276	11.218
τ (s^{-1})	0.609	0.346	0.173	0.121	0.089
1/n ln(k)	-0.638	-1.204	-1.897	-2.254	-2.555

Crystallization Activation Energy Summary

	Neat PP	PP_Nano_MB	PP_Nano_Powder	Polypropylene
	ΔE kJ mol-1	**ΔE kJ mol-1**	**ΔE kJ mol-1**	
Malkin	-364.8	**-385.2**	**-388.1**	**-265.8**
Avrami Non Linear	-366.3	**-385.6**	**-382.0**	**-264.8**
Isoconversional				
X(t)				
0.01	-406.75	**-372.0**	**-386.1**	**-243.3**
0.02	-414.01	**-413.4**	**-387.0**	**-196.2**
0.03	-403.30	**-406.2**	**-374.6**	**-229.2**
0.04	-400.31	**-429.9**	**-368.4**	**-254.1**
0.05	-395.51	**-426.8**	**-367.9**	**-237.0**
0.06	-392.86	**-420.9**	**-372.3**	**-258.5**
0.07	-390.69	**-404.9**	**-364.4**	**-243.7**
0.08	-392.74	**-408.7**	**-363.7**	**-235.5**
0.09	-392.75	**-412.9**	**-371.2**	**-255.2**
0.1	-381.95	**-412.7**	**-361.8**	**-245.4**
0.2	-368.07	**-387.5**	**-363.9**	**-254.1**
0.3	-356.67	**-375.9**	**-369.7**	**-253.3**
0.4	-360.00	**-376.3**	**-376.5**	**-255.2**
0.5	-349.54	**-377.6**	**-386.2**	**-257.9**
0.6	-341.78	**-368.0**	**-392.3**	**-264.3**
0.7	-323.04	**-375.3**	**-403.8**	**-270.4**
0.8	-310.77	**-367.3**	**-403.8**	**-273.5**
0.9	-392.14	**-358.2**	**-454.7**	**-312.8**

Comparison of Activation Energy – Isoconversional Method



Experimental: Results - Interpretation of Data

- Neat PP
  - Sample is nucleated with a ΔE value of ~ -365 kJ / mol compared to the control PP value of -285 kJ / mol
  - Rate constants are consistently higher than the control
  - Avrami exponent 'n' is generally closer to 2 except in once case. This is likely due to poor dispersion.
  - Malkin C_0 is consistently lower except in one case due to dispersion. This indicates nucleation is predominantly propagation of new crystal sites.
- Nan-O-Sil Powder
  - Sample shows activation energy of ~ -385 kJ / mol – lower than the Neat PP and significantly lower than the polypropylene reference.
  - Rate constants are significantly higher
  - Avrami exponent 'n' is close to 2 in most cases but does approach get higher in one case due to dispersion issues.
  - Malkin C_0 is consistently lower except in one case due to dispersion

Experimental: Results - Interpretation of Data

- Control Polypropylene
  - Typical behavior of polypropylene with a Avrami exponent 'n' of ~ 3 and relatively high Malkin C_0 constant.
  - ΔE in typical range ~ -280 kJ / mol for non-nucleated PP
- Nan-O-Sil Master batch
  - Sample shows activation energy of ~ -385 kJ / mol which represent a significant lowering of activation energy
  - Despite the low ΔE, the rate constants are lower. This is due to a Avrami exponent 'n' value of ~ 3. Nucleation efficiency in PP seems to be optimal at 'n' = 2.
  - Malkin C_0 is relatively high indicating the predominant nucleation mechanism is propagation of existing crystal domains
  - Master batch behaves like some mineral fillers (talc for example) giving a lower activation energy and some improvement in cycle time, but with a spherical geometry.
  - Typically nucleators will have optimal concentrations levels.

Conclusions

- The Q 2000 DSC is the optimal tool for assessing nucleator performance in polypropylene and other plastics. This is due to several factors including:
  - Tzero baseline performance – a flat baseline is critical in isothermal studies, and the baseline performance is superior.
  - Reliable autosampler
  - Ease of calibration
- The Nan-O-Sil additive has a significant nucleation effect on polypropylene as indicated by the lowering of activation energy, improved rate constants, change in Avrami geometric exponent ‘n’ and lower value of Malkin C_0.
- All of this should result in improved cycle times in processing PP.

Thank You

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