APPENDIX A:

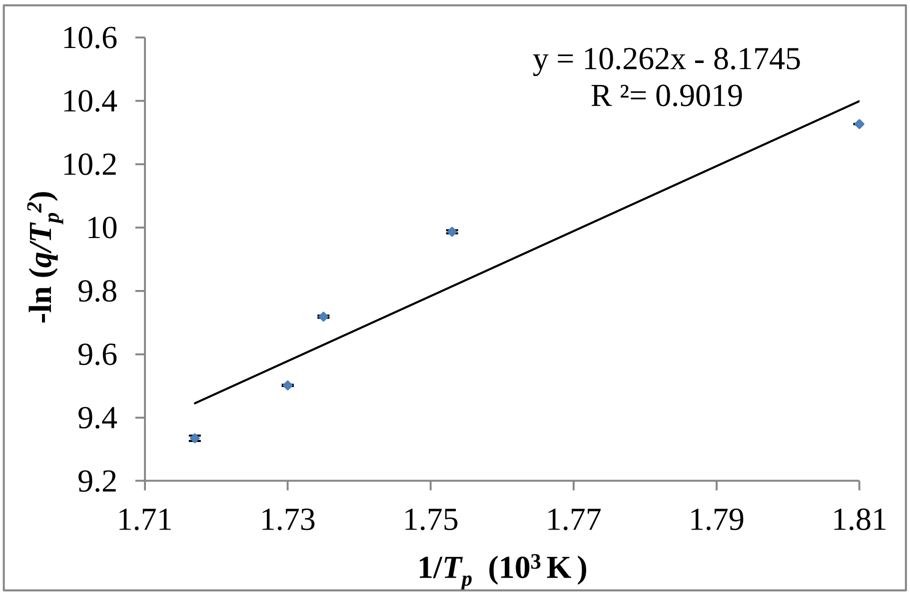
Determination of kinetic parameters for mcl-PHA during thermal degradation

A.1 Descriptions of calculations of E_d, A and ΔS for OA-derived PHA

q (K min^{-1})	T_p (K)		$1/T_p$ (x10^{-3} K^{-1})		T_p^2 (K^2)		q/T_p^2 (10^{-5} min^{-1} K^{-1})		$-\ln(q/T_p^2)$	
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
10	550.8	554.1	1.82	1.81	303413.69	306971.40	3.30	3.26	10.32	10.33
15	571.0	570.2	1.75	1.75	326086.68	325150.85	4.60	4.61	9.99	9.98
20	577.2	575.6	1.73	1.74	333125.21	331303.85	6.00	6.04	9.72	9.72
25	579.1	577.1	1.73	1.73	335368.39	333032.87	7.45	7.51	9.50	9.50
30	582.6	582.3	1.72	1.712	339422.76	339038.35	8.84	8.85	9.33	9.33

Average of 2 replicates:

q (K min^{-1})	$1/T_p$ (x10^3 K)	$-\ln(q/T_p^2)$
10	1.81	10.33
15	1.75	9.99
20	1.74	9.72
25	1.73	9.50
30	1.72	9.33



Equation for the Kissinger plot: Y = 10.262X -8.1745

Calculations of E_d and A for OA-derived PHA:

With gradient, $E_d/R = 10.262 \times 10^3$ K

$E_d = 10262$ K x 8.3143 $JK^{-1}mol^{-1}$

= 85321.3466 J mol^{-1}

= 85.3 kJ mol^{-1}

With intersection of y-axis, ln $(AR/E_d) = 8.1745$

$AR/E_d = e^{8.1745}$

$A = E_d/R \times e^{8.1745}$

$= 10.262 \times 10^3 \times e^{8.1745}$ min^{-1}

= 36,422,709.72 min^{-1}

=36,422,709.72 /60 s^{-1}

= 607,045.162 s^{-1}

= 6.07 $x10^5$ s^{-1}

Calculation of ∆S for OA-derived PHA:

At heating rate of 10 K min^{-1},

ΔS= 8.3143 x ln $(6.07x10^5)(6.626x10^{-34})/(1.3807x10^{-23})(552.44)$

= 8.3143x ln $(2.9x10^{-5})/(552.44)$

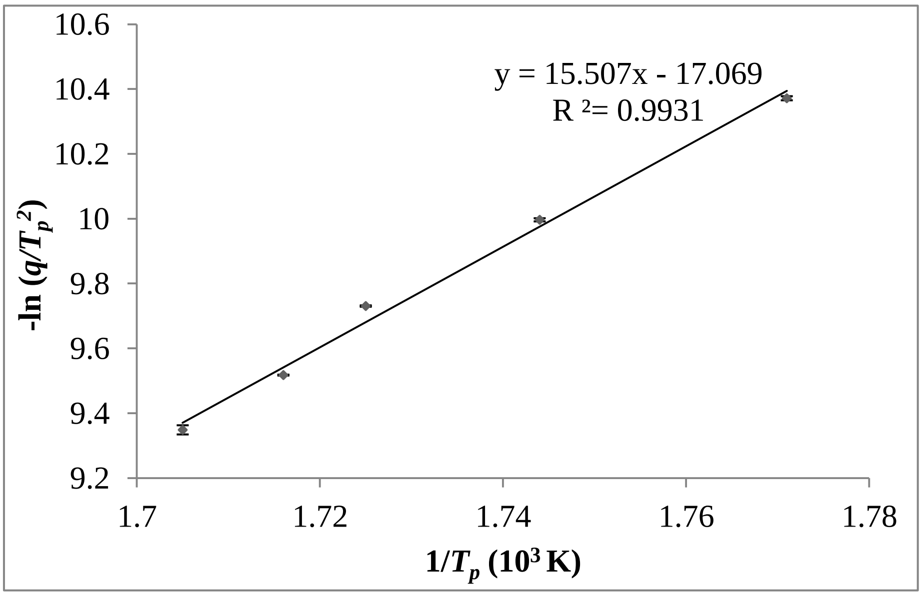
= -139.4 J K^{-1} mol^{-1}

A.2 Descriptions of calculations of E_d, A and ΔS for SPKO-derived PHA

q (K min^{-1})	T_p (K)		$1/T_p$ (x10^{-3} K^{-1})		T_p^2 (K^2)		q/T_p^2 (10^{-5} min^{-1} K^{-1})		-ln(q/T_p^2)	
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
10	563.4	566.2	1.78	1.77	317453.36	320548.47	3.15	3.12	10.37	10.36
15	572.5	574.6	1.75	1.74	327699.00	330211.13	4.58	4.54	9.99	10.00
20	579.4	580.2	1.73	1.72	335739.12	336597.23	5.96	5.94	9.73	9.73
25	583.1	582.5	1.72	1.72	340040.60	339282.95	7.35	7.37	9.52	9.52
30	589.8	583.8	1.70	1.71	347828.65	340845.79	8.63	8.80	9.36	9.34

Average of 2 replicates:

q (K min^{-1})	$1/T_p$ (x10^3 K)	-ln(q/T_p^2)
10	1.77	10.37
15	1.74	10.00
20	1.73	9.73
25	1.72	9.52
30	1.71	9.35



Equation for the Kissinger plot: Y = 15.507X – 17.069

Calculations of E_d and A for SPKO-derived PHA:

With gradient, $E_d/R = 15.507 \times 10^3$ K

$E_d = 15507$ K x 8.3143 J K^{-1} mol^{-1}

= 128929.8501 J mol^{-1}

= 128.9 kJ mol^{-1}

With intersection of y-axis, ln $(AR/E_d) = 17.069$

$AR/E_d = e^{17.609}$

$A = E_d/R \times e^{17.609}$

$= 15.507 \times 10^3 \times e^{17.609} min^{-1}$

$= 6.89 \times 10^{11}$ min^{-1}

$= 6.89 \times 10^{11}/60$ s^{-1}

$= 1.15 \times 10^{10}$ s^{-1}

Calculation of ΔS for SPKO-derived PHA:

At heating rate of 10 K min^{-1},

$\Delta S = 8.3143 \times \ln (1.15\times10^{10})(6.626\times10^{-34})/(1.3807\times10^{-23})(564.8)$

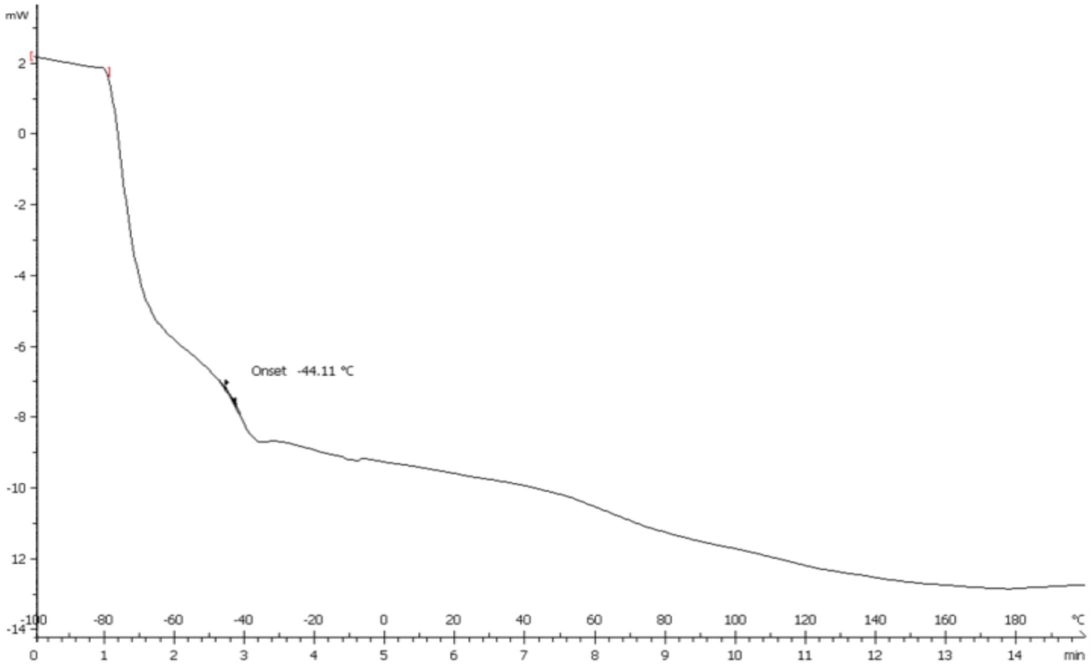
$= 8.3143 \times \ln (5.52\times10^{-1})/(564.8)$

$= -57.6$ J K^{-1} mol^{-1}

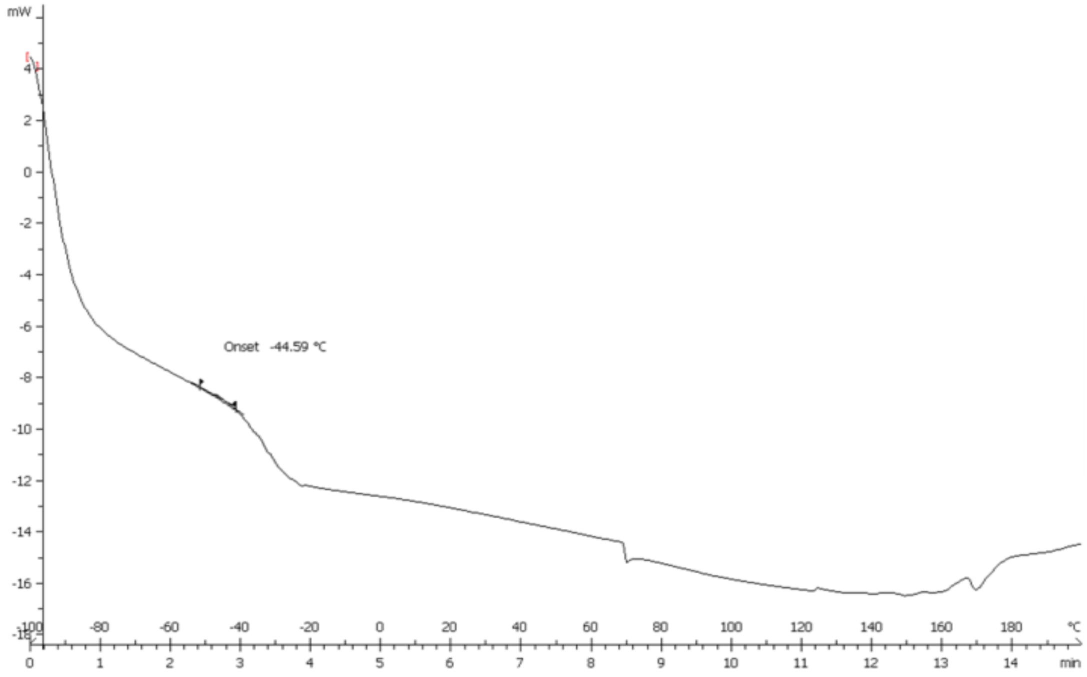
APPENDIX B:

DSC thermograms of undegraded and heat-treated mcl-PHA

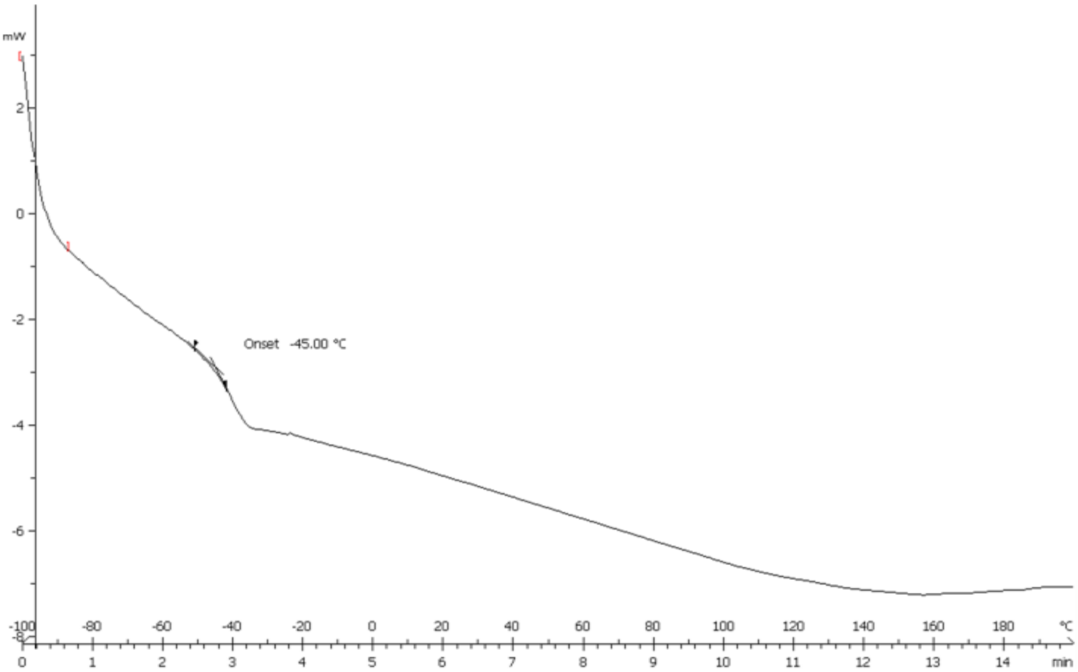
B.1 DSC thermogram of OA-derived PHA



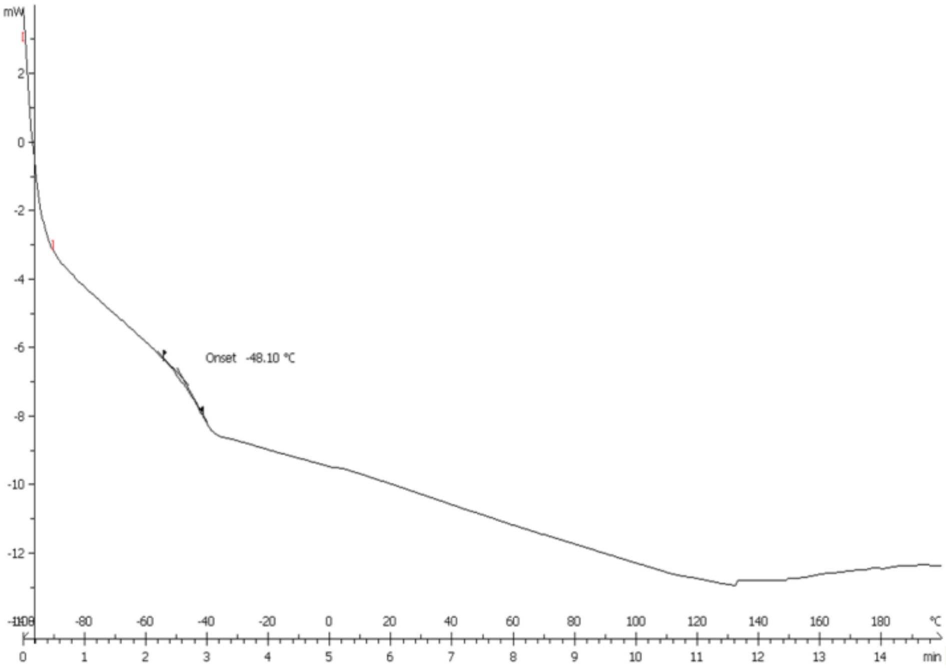
B.2 DSC thermogram of 160 ℃-treated OA-derived PHA



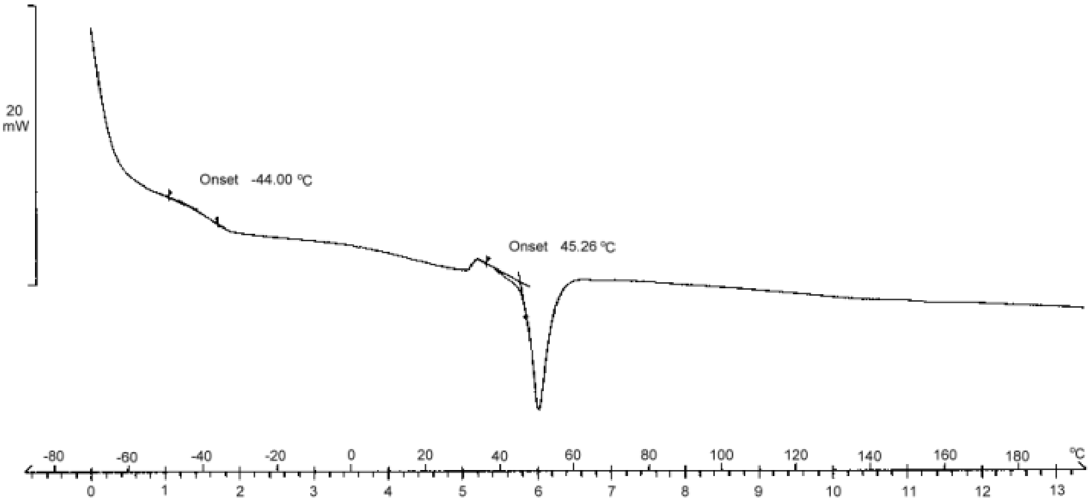
B.3 DSC thermogram of 170 ℃-treated OA-derived PHA



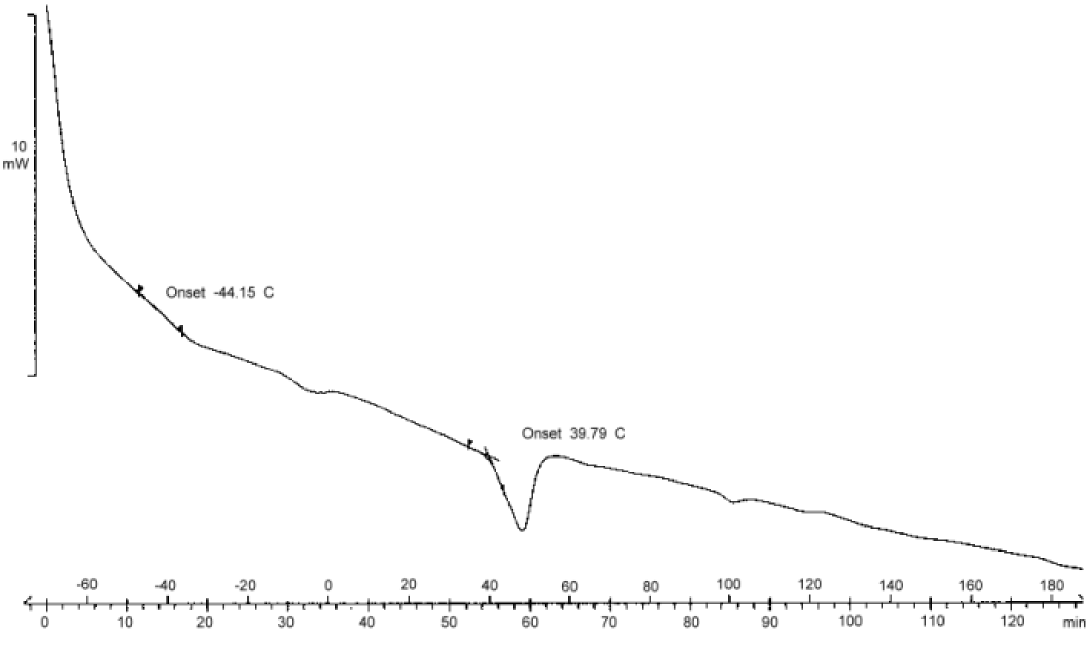
B.4 DSC thermogram of 180 ℃-treated OA-derived PHA



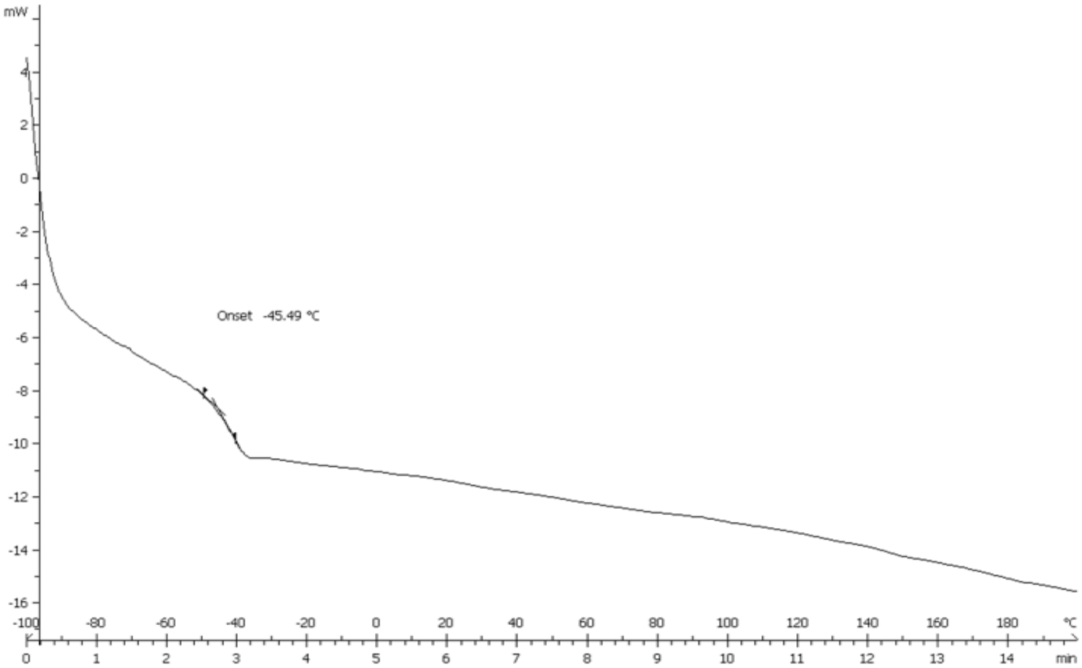
B.5 DSC thermogram of SPKO-derived PHA



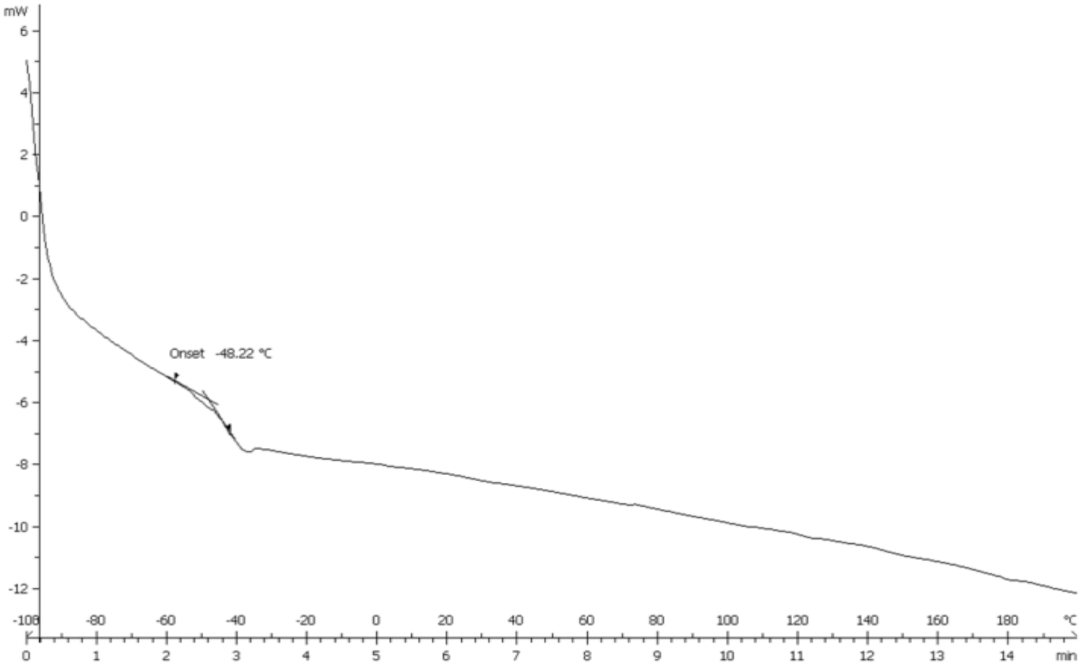
B.6 DSC thermogram of 160 ℃-treated SPKO-derived PHA



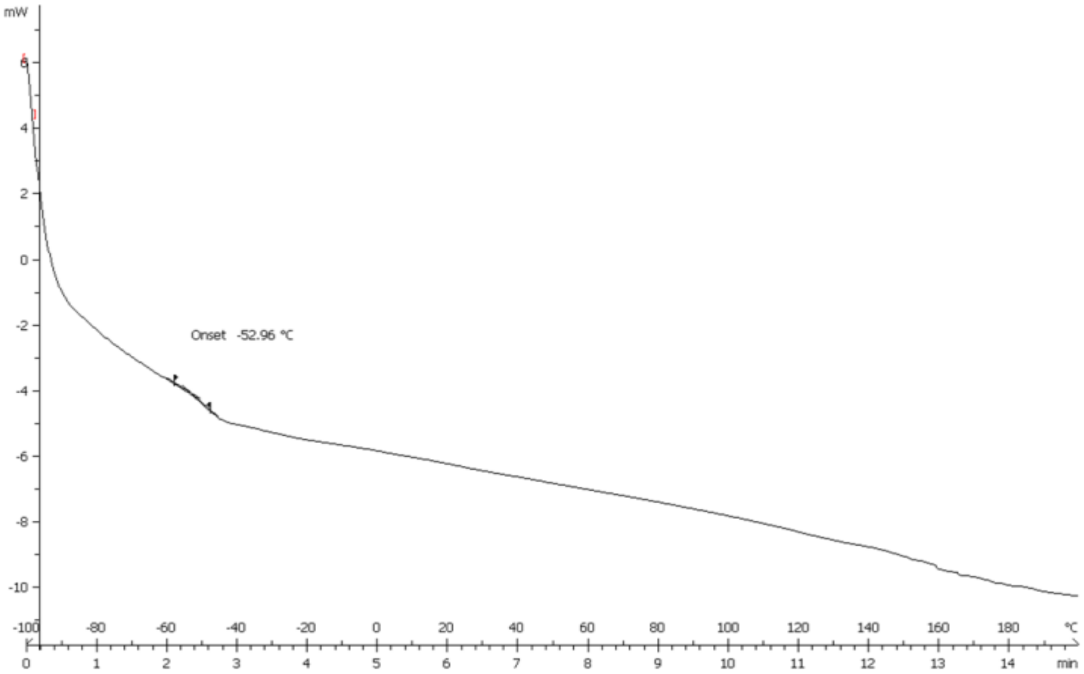
B.7 DSC thermogram of 170 ℃-treated SPKO-derived PHA



B.8 DSC thermogram of 180 ℃-treated SPKO-derived PHA



B.9 DSC thermogram of 190 ℃-treated SPKO-derived PHA



APPENDIX C:

Determination of acid number, M_n and concentrations of -COOH end groups for mcl-PHA before and thermal treatments

C.1 Calculation of acid number for OA-derived PHA before and after thermal treatments

1) Preparation of KOH/EtOH solution

M_w of KOH = 56.11 g mol^{-1}

1.1756 g KOH was dissolved in 1 L 95% Ethanol (EtOH)

$$\text{No. of moles} = \frac{1.1756\ \text{g}}{56.11\ \text{g mol}^{-1}}$$

$$= 0.021\ \text{mol}$$

$$N_{\text{KOH}} = 0.021\text{mol dm}^{-3}$$

$$= 0.021\ \text{M}$$

$$= 0.02\ \text{N}$$

2) Standardization of KOH with KHP

KHP weight rep.1 = 108.0536 g – 108.0706 g = 0.0170 g

KHP weight rep.2 = 83.3810 g – 83.3655 g = 0.0155 g

50 mL KHP (in dH_2O) titrated with KOH

KOH volume rep.1 = 29.10 mL – 17.05 mL = 12.05 mL

KOH volume rep.2 = 49.80 mL – 38.80 mL = 11.00 mL

$$N_{\text{KOH rep. 1}} = \frac{0.0170\ \text{g}}{12.05\ \text{mL x } 0.2042} \qquad N_{\text{KOH rep. 2}} = \frac{0.0155\ \text{g}}{11.00\ \text{mL x } 0.2042}$$

$$= 0.00691\ \text{N} \qquad = 0.0069\ \text{N}$$

Thus, Average N_{KOH} = 0.0069 N

3) Blank titration with KOH

(50ml toluene/EtOH solution titrated with 0.0069 N KOH)

Replicate 1: Volume of KOH before titration = 24.30 mL

Volume of KOH after titration = 23.00 mL

Volume of KOH used = 1.30 mL

Replicate 2: Volume of KOH before titration = 28.10 mL

Volume of KOH after titration = 26.75 mL

Volume of KOH used = 1.35 mL

Thus, Average KOH volume for blank titration = 1.325 mL

Determination of acid number for OA-derived PHA before thermal treatment:

PHA samples were dissolved in 50 mL of toluene & EtOH solution in the ratio of 2:1 and titrated with KOH

Total toluene & EtOH volume =1 L

Volume of toluene = 2/3 x 1 L = 666.7 mL
Volume of EtOH = 1/3 x 1 L = 333.3 mL

Weight of titrated PHA rep.1 = 126.3730 g – 126.0513 g = 0.3217 g
Weight of titrated PHA rep.2 = 125.6419 g – 125.3205 g = 0.3214 g

Volume of KOH used for titration rep.1 = 32.80-28.10 = 4.70 mL
Volume of KOH used for titration rep.2 = 37.65-33.00 = 4.65 mL

PHA weight rep.1 = 0.3217 g ; KOH volume used = 4.70 mL
PHA weight rep.2 = 0.3214 g ; KOH volume used = 4.65 mL

V_{blank} = 1.325 mL
Average N_{KOH} = 0.0069 N

$$\text{Acid number } (AN) = \frac{56.1 \times N \times (V - V_{\mathrm{blank}})}{W_{\mathrm{PHA}}}$$

$$AN_{\mathrm{rep.1}} = \frac{56.1 \times 0.0069 \times (4.70-1.325)}{0.3217} \qquad AN_{\mathrm{rep.2}} = \frac{56.1 \times 0.0069 \times (4.65-1.325)}{0.3214}$$

$$= 4.07 \text{ mg KOH g}^{-1} \qquad = 4.01 \text{ mg KOH g}^{-1}$$

So, AN_{average} = 4.04 mg KOH g^{-1}

Determination of acid number for 160 °C-treated OA-derived PHA:

Weight of titrated PHA rep.1 = 125.0240 g – 124.7209 g = 0.3031 g
Weight of titrated PHA rep.2 = 133.7348 g – 133.5855 g = 0.1493 g

Volume of KOH used for titration rep.1 = 43.25 mL – 37.80 mL = 5.45 mL
Volume of KOH used for titration rep.2 = 46.60 mL – 43.25 mL = 3.35 mL

PHA weight rep.1 = 0.3031 g ; KOH volume used = 5.45 mL
PHA weight rep.2 = 0.1493 g ; KOH volume used = 3.35 mL

$V_{\text{blank}} = 1.325$ mL
Average $N_{\text{KOH}} = 0.0069$ N

$$AN_{\text{rep.1}} = \frac{56.1 \times 0.0069 \times (5.45-1.325)}{0.3031} \qquad AN_{\text{rep.2}} = \frac{56.1 \times 0.0069 \times (3.35-1.325)}{0.1493}$$

$$= 5.28 \text{ mg KOH g}^{-1} \qquad = 5.26 \text{ mg KOH g}^{-1}$$

So, $AN_{\text{average}} = 5.27$ mg KOH g^{-1}

Determination of acid number for 170 °C-treated OA-derived PHA:

Weight of titrated PHA rep.1 = 120.9833 g – 120.7897 g = 0.1936 g
Weight of titrated PHA rep.2 = 111.9622 g – 111.7616 g = 0.2006 g

Volume of KOH used for titration rep.1 = 31.30 mL - 22.70 mL = 8.60 mL
Volume of KOH used for titration rep.2 = 43.80 mL - 34.95 mL = 8.85 mL

PHA weight rep.1 = 0.1936 g ; KOH volume used = 8.60 mL
PHA weight rep.2 = 0.2006 g ; KOH volume used = 8.85 mL

$V_{\text{blank}} = 1.325$ mL
Average $N_{\text{KOH}} = 0.0069$ N

$$AN_{\text{rep.1}} = \frac{56.1 \times 0.0069 \times (8.60-1.325)}{0.1936} \qquad AN_{\text{rep.2}} = \frac{56.1 \times 0.0069 \times (8.85-1.325)}{0.2006}$$

$$= 14.56 \text{ mg KOH g}^{-1} \qquad = 14.53 \text{ mg KOH g}^{-1}$$

So, $AN_{\text{average}} = 14.55$ mg KOH g^{-1}

Determination of acid number for 180 ℃-treated OA-derived PHA:

Note: KOH/EtOH solution used in the titration for 180 ℃-treated OA-PHA is different from the KOH/EtOH solution used in the titration for the rest of the PHA samples (different normality)

Weight of titrated PHA rep.1 = 94.7307 g – 94.5042 g = 0.2265 g
Weight of titrated PHA rep.2 = 93.7325 g – 93.5258 g = 0.2067 g

Volume of KOH used for titration rep.1 = 30.40 mL – 9.50 mL = 20.90 mL
Volume of KOH used for titration rep.2 = 36.00 mL – 16.60 mL = 19.40 mL

PHA weight rep.1 = 0.2265 g ; KOH volume used = 20.90 mL
PHA weight rep.2 = 0.2067 g ; KOH volume used = 19.40 mL

$V_{\text{blank}} = 1.325$ mL
Average $N_{\text{KOH}} = 0.00679$ N

$$AN_{\text{rep.1}} = \frac{56.1 \text{ x } 0.00679 \text{ N x } (20.9\text{-}1.325) \text{ mL}}{0.2265 \text{ g}}$$

$= 32.92$ mg KOH g^{-1}

$$AN_{\text{rep.2}} = \frac{56.1 \text{ x } 0.00679 \text{ N x } (19.4\text{-}1.325) \text{ mL}}{0.2067 \text{ g}}$$

$= 33.30$ mg KOH g^{-1}

So, $AN_{\text{average}} = 33.11$ mg KOH g^{-1}

C.2 Calculation of acid number for SPKO-derived PHA before and after thermal treatments

1) Standardization of KOH with KHP

KHP weight rep.1 = 116.3690 g – 116.3347 g = 0.0343 g

KHP weight rep.2 = 83.4117 g – 83.3884 g = 0.0233 g

50 mL KHP (in dH_2O) titrated with KOH

KOH volume rep.1 = 37.50 mL – 20.80 mL = 16.70 mL

KOH volume rep.2 = 48.40 mL – 24.70 mL = 23.70 mL

$$N_{\text{KOH rep. 1}} = \frac{0.0233\ \text{g}}{16.70\ \text{mL} \times 0.2042} = 0.00683\ \text{N} \qquad N_{\text{KOH rep. 2}} = \frac{0.0343\ \text{g}}{23.70\ \text{mL} \times 0.2042} = 0.00709\ \text{N}$$

Thus, Average N_{KOH} = 0.00696 N

2) Blank titration with KOH

(50ml toluene/EtOH solution titrated with 0.00696 N KOH)

Replicate 1: Volume of KOH before titration = 34.05 mL
Volume of KOH after titration = 32.80 mL
Volume of KOH used = 1.25 mL

Replicate 2: Volume of KOH before titration = 35.65 mL
Volume of KOH after titration = 34.25 mL
Volume of KOH used = 1.40 mL

Thus, Average KOH volume used for blank titration = 1.325 mL

Determination of acid number for SPKO-derived PHA before thermal treatment:

Weight of titrated PHA rep.1 = 94.9326 g – 94.5062 g = 0.4264 g
Weight of titrated PHA rep.2 = 93.9255 g – 93.5288 g = 0.3967 g

Volume of KOH used for titration rep.1 = 27.65-20.70 = 6.95 mL
Volume of KOH used for titration rep.2 = 34.45-27.90 = 6.55 mL

PHA weight rep.1 = 0.4264 g ; KOH volume used = 6.95 mL
PHA weight rep.2 = 0.3967 g ; KOH volume used = 6.55 mL

$V_{\text{blank}} = 1.325$ mL
Average $N_{\text{KOH}} = 0.00696$ N

$$\text{Acid number } (AN) = \frac{56.1 \text{ x } N \text{ x } (V-V_{\text{blank}})}{W_{\text{PHA}}}$$

$$AN_{\text{rep.1}} = \frac{56.1 \text{ x } 0.00696 \text{ x } (6.95-1.325)}{0.4264} \qquad AN_{\text{rep.2}} = \frac{56.1 \text{ x } 0.00696 \text{ x } (6.55-1.325)}{0.3967}$$

$$= 5.15 \text{ mg KOH g}^{-1} \qquad = 5.14 \text{ mg KOH g}^{-1}$$

So, $AN_{\text{average}} = 5.15$ mg KOH g^{-1}

Determination of acid number for 160 ℃-treated SPKO-derived PHA

Note: KOH/EtOH solution used in the titration for 160 ℃-treated SPKO-PHA is different from the KOH/EtOH solution used in the titration for the rest of the PHA samples (different normality)

KHP weight rep.1 = 116.3662 g – 116.3335 g = 0.0327 g
KHP weight rep.2 = 83.4315 g – 83.3872 g = 0.0443 g

KOH volume rep.1 = 37.55 mL – 21.10 mL = 16.45 mL
KOH volume rep.2 = 48.30 mL – 25.50 mL = 22.80 mL

$$N_{\text{KOH rep. 1}} = \frac{0.0327\text{ g}}{16.45\text{ mL x }0.2042} = 0.00973\text{ N} \qquad N_{\text{KOH rep. 2}} = \frac{0.0443\text{ g}}{22.80\text{ mL x }0.2042} = 0.00952\text{ N}$$

Thus, Average N_{KOH} = 0.00962 N

Weight of titrated PHA rep.1 = 94.6540 g – 94.5078 g = 0.1462 g
Weight of titrated PHA rep.2 = 83.5374 g – 83.3880 g = 0.1494 g

Volume of KOH used for titration rep.1 = 11.60 mL - 8.50 mL = 3.10 mL
Volume of KOH used for titration rep.2 = 14.80 mL – 11.60 mL = 3.20 mL

PHA weight rep.1 = 0.1462 g ; KOH volume used = 3.10 mL
PHA weight rep.2 = 0.1494 g ; KOH volume used = 3.20 mL

V_{blank} = 1.325 mL
Average N_{KOH} = 0.00962 N

$$AN_{\text{rep.1}} = \frac{56.1\text{ x }0.00962\text{ x }(3.10-1.325)}{0.1462} = 6.55\text{ mg KOH g}^{-1} \qquad AN_{\text{rep.2}} = \frac{56.1\text{ x }0.00962\text{ x }(3.20-1.325)}{0.1494} = 6.77\text{ mg KOH g}^{-1}$$

So, AN_{average} = 6.66 mg KOH g^{-1}

Determination of acid number for 170 ℃-treated SPKO-derived PHA:

Weight of titrated PHA rep.1 = 108.2775 g – 108.0530 g = 0.2245 g
Weight of titrated PHA rep.2 = 107.7077 g – 107.4497 g = 0.2580 g

Volume of KOH used for titration rep.1 = 25.05 mL – 19.15 mL = 5.90 mL
Volume of KOH used for titration rep.2 = 31.10 mL – 24.55 mL = 6.55 mL

PHA weight rep.1 = 0.2245 g ; KOH volume used = 5.90 mL
PHA weight rep.2 = 0.2580 g ; KOH volume used = 6.55 mL

V_{blank} = 1.325 mL
Average N_{KOH} = 0.00696 N

$$AN_{\text{rep.1}} = \frac{56.1 \text{ x } 0.00696 \text{ x } (5.90-1.325)}{0.2245} \qquad AN_{\text{rep.2}} = \frac{56.1 \text{ x } 0.00696 \text{ x } (6.55-1.325)}{0.2580}$$

$$= 7.96 \text{ mg KOH g}^{-1} \qquad = 7.91 \text{ mg KOH g}^{-1}$$

So, AN_{average} = 7.94 mg KOH g^{-1}

Determination of acid number for 180 ℃-treated OA-derived PHA:

Weight of titrated PHA rep.1 = 116.5483 g – 116.3331 g = 0.2152 g
Weight of titrated PHA rep.2 = 83.6075 g – 83.3863 g = 0.2212 g

Volume of KOH used for titration rep.1 = 40.70 mL – 32.45 mL = 8.25 mL
Volume of KOH used for titration rep.2 = 49.00 mL – 40.70 mL = 8.30 mL

PHA weight rep.1 = 0.2152 g ; KOH volume used = 8.25 mL
PHA weight rep.2 = 0.2212 g ; KOH volume used = 8.30 mL

V_{blank} = 1.325 mL
Average N_{KOH} = 0.00696 N

$$AN_{\text{rep.1}} = \frac{56.1 \text{ x } 0.00696 \text{ x } (8.25-1.325)}{0.2152} \qquad AN_{\text{rep.2}} = \frac{56.1 \text{ x } 0.00696 \text{ x } (8.30-1.325)}{0.2212}$$

$$= 12.56 \text{ mg KOH g}^{-1} \qquad = 12.31 \text{ mg KOH g}^{-1}$$

So, AN_{average} = 12.44 mg KOH g^{-1}

Determination of acid number for 190 ℃-treated OA-treated PHA:

Weight of PHA replicate 1 = 94.6986 g – 94.5064 g = 0.1922 g
Weight of PHA replicate 2 = 83.5800 g – 83.3839 g = 0.1961 g

KOH volume used rep.1 = 46.70 mL – 27.80 mL = 18.90 mL
KOH volume used rep.2 = 33.35 mL – 14.50 mL = 18.85 mL

PHA weight rep.1 = 0.1922 g ; KOH volume used = 18.90 mL
PHA weight rep.2 = 0.1961 g ; KOH volume used = 18.85 mL

$V_{\text{blank}} = 1.325$ mL
Average $N_{\text{KOH}} = 0.00696$ N

$$AN_{\text{rep.1}} = \frac{56.1 \text{ x } 0.00696 \text{ x } (18.90-1.325)}{0.1922} \qquad AN_{\text{rep.2}} = \frac{56.1 \text{ x } 0.00696 \text{ x } (18.85-1.325)}{0.1961}$$

$$= 35.70 \text{ mg KOH g}^{-1} \qquad = 34.89 \text{ mg KOH g}^{-1}$$

So, $AN_{\text{average}} = 35.30$ mg KOH g^{-1}

C.3 Calculation of M_n for OA-derived PHA before and after thermal treatments

Since Acid Number (*AN*) is the number of mg of KOH necessary to neutralize the free fatty acids in 1 g of PHA and the number of moles of PHA equals to the number of moles of COOH (also equals to number of moles of KOH)

Therefore,

$$M_n = \frac{\text{weight of PHA sample}}{\text{no. of moles of COOH group}}$$

$$= \frac{1}{\frac{\text{Acid number x } 10^{-3}}{56.11}}$$

$$= \frac{56100}{\text{Acid number}}$$

For OA-derived PHA:

Rep 1: M_n = 56100/4.07 = 13783.78

Rep 2: M_n = 56100/4.01 = 13990.02

M_n average = 13886.9 g $\text{mol}^{-1} \approx$ 13900 g mol^{-1}

For 160 °C-treated OA-derived PHA:

Rep 1: M_n = 56100/5.28 = 10625.00

Rep 2: M_n = 56100/5.26 = 10665.40

M_n average = 10645.2 g $\text{mol}^{-1} \approx$ 10600 g mol^{-1}

For 170 °C-treated OA-derived PHA:

Rep 1: M_n = 56100/14.56 = 3853.02

Rep 2: M_n = 56100/14.53 = 3860.98

M_n average = 3857.0 g $\text{mol}^{-1} \approx$ 3900 g mol^{-1}

For 180 °C-treated OA-derived PHA:

Rep 1: M_n = 56100/32.92 = 1704.13

Rep 2: M_n = 56100/33.31 = 1684.18

M_n average = 1694.16 g $\text{mol}^{-1} \approx$1700 g mol^{-1}

C.4 Calculation of M_n for SPKO-derived PHA before and after thermal treatments

For SPKO-derived PHA:

Rep 1: M_n = 56100/5.14 = 10914.40
Rep 2: M_n = 56100/5.15 = 10893.20

M_n average = 10903.80 g $mol^{-1} \approx$ 10900 g mol^{-1}

For 160 ℃-treated SPKO-derived PHA:

Rep 1: M_n = 56100/6.55 = 8564.89
Rep 2: M_n = 56100/6.77 = 8286.56

M_n average = 8425.73 g $mol^{-1} \approx$ 8400 g mol^{-1}

For 170 ℃-treated SPKO-derived PHA:

Rep 1: M_n = 56100/7.96 = 7047.74
Rep 2: M_n = 56100/7.91 = 7092.29

M_n average = 7070.02 g $mol^{-1} \approx$ 7100 g mol^{-1}

For 180 ℃-treated SPKO-derived PHA:

Rep 1: M_n = 56100/12.56 = 4466.56
Rep 2: M_n = 56100/12.31 = 4557.27

M_n average = 4511.92 g $mol^{-1} \approx$4500 g mol^{-1}

For 190 ℃-treated SPKO-derived PHA:

Rep 1: M_n = 56100/35.70 = 1571.43
Rep 2: M_n = 56100/34.89 = 1607.92

M_n average = 1589.68 g $mol^{-1} \approx$1600 g mol^{-1}

C.5 Calculation of concentrations of -COOH end groups in OA-derived PHA before and after thermal treatments

No. of moles of poly(hydroxyalkanoate) units = no. of moles of -COOH end groups
= no. of moles of KOH
= $1/M_n$
= Acid number/ 56100

For OA-derived PHA:

Rep 1: No. of moles of -COOH group = 4.07/56100 = 7.25×10^{-5} moles
Rep 2: No. of moles of -COOH group = 4.01/56100 = 7.15×10^{-5} moles

Average no. of moles of -COOH group = 7.20×10^{-5} moles
Concentration of -COOH end groups in 1 g of PHA = 7.2×10^{-5} mol g^{-1}

For 160 °C-treated OA-derived PHA:

Rep 1: No. of moles of -COOH group = 5.28/56100 = 9.41×10^{-5} moles
Rep 2: No. of moles of -COOH group = 5.26/56100 = 9.38×10^{-5} moles

Average no. of moles of -COOH group = 9.40×10^{-5} moles
Concentration of -COOH end groups in 1 g of PHA = 9.4×10^{-5} mol g^{-1}

For 170 °C-treated OA-derived PHA:

Rep 1: No. of moles of -COOH group = 14.56/56100 = 2.60×10^{-5} moles
Rep 2: No. of moles of -COOH group = 14.53/56100 = 2.59×10^{-5} moles

Average no. of moles of -COOH group = 2.60×10^{-5} moles
Concentration of -COOH end groups in 1 g of PHA = 2.60×10^{-5} mol g^{-1}

For 180 °C-treated OA-derived PHA:

Rep 1: No. of moles of -COOH group = 32.92/56100 = 5.87×10^{-5} moles
Rep 2: No. of moles of -COOH group = 33.31/56100 = 5.94×10^{-5} moles

Average no. of moles of -COOH group = 5.91×10^{-3} moles
Concentration of -COOH end groups in 1 g of PHA = 5.9×10^{-3} mol g^{-1}

C.6 Calculation of concentrations of -COOH end groups in SPKO-derived PHA before and after thermal treatments

For SPKO-derived PHA:

Rep 1: No. of moles of -COOH group = 5.15/56100 = 9.18 x 10^{-5} moles
Rep 2: No. of moles of -COOH group = 5.14/56100 = 9.16 x 10^{-5} moles

Average no. of moles of -COOH group = 9.17 x 10^{-5} moles
Concentration of -COOH end groups in 1 g of PHA = 9.2 x 10^{-5} mol g^{-1}

For 160 °C-treated SPKO-derived PHA:

Rep 1: No. of moles of -COOH group = 6.55/56100 = 1.17 x 10^{-5} moles
Rep 2: No. of moles of -COOH group = 6.77/56100 = 1.21 x 10^{-5} moles

Average no. of moles of -COOH group = 1.19 x 10^{-5} moles
Concentration of -COOH end groups in 1 g of PHA = 1.2 x 10^{-5} mol g^{-1}

For 170 °C-treated SPKO-derived PHA:

Rep 1: No. of moles of -COOH group = 7.96/56100 = 1.42 x 10^{-5} moles
Rep 2: No. of moles of -COOH group = 7.91/56100 = 1.41 x 10^{-5} moles

Average no. of moles of -COOH group = 1.42 x 10^{-5} moles
Concentration of -COOH end groups in 1 g of PHA = 1.42 x 10^{-5} mol g^{-1}

For 180 °C-treated SPKO-derived PHA:

Rep 1: No. of moles of -COOH group = 12.56/56100 = 2.24 x 10^{-5} moles
Rep 2: No. of moles of -COOH group = 12.31/56100 = 2.19 x 10^{-5} moles

Average no. of moles of -COOH group = 2.22 x 10^{-3} moles
Concentration of -COOH end groups in 1 g of PHA = 2.2 x 10^{-3} mol g^{-1}

For 190 °C-treated SPKO-derived PHA:

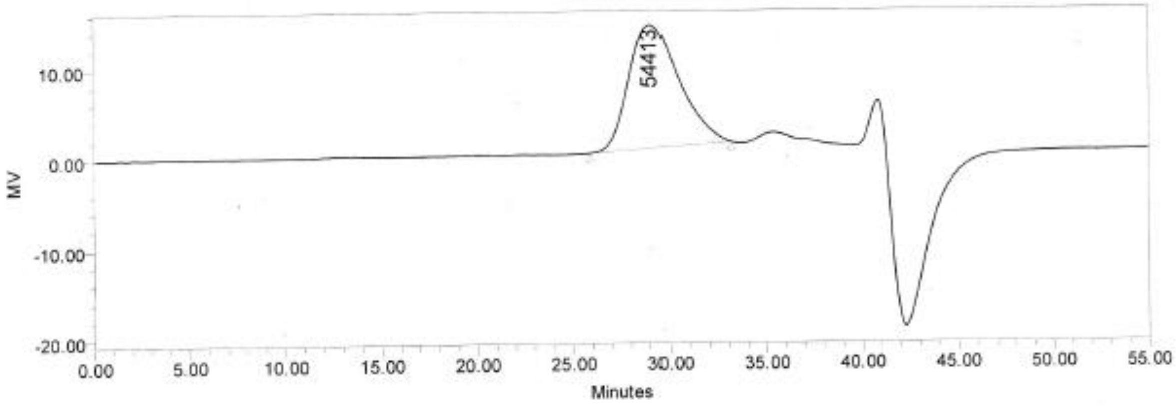
Rep 1: No. of moles of -COOH group = 35.70/56100 = 6.36 x 10^{-5} moles
Rep 2: No. of moles of -COOH group = 34.89/56100 = 6.22 x 10^{-5} moles

Average no. of moles of -COOH group = 6.29 x 10^{-3} moles
Concentration of -COOH end groups in 1 g of PHA = 6.3 x 10^{-3} mol g^{-1}

APPENDIX D:

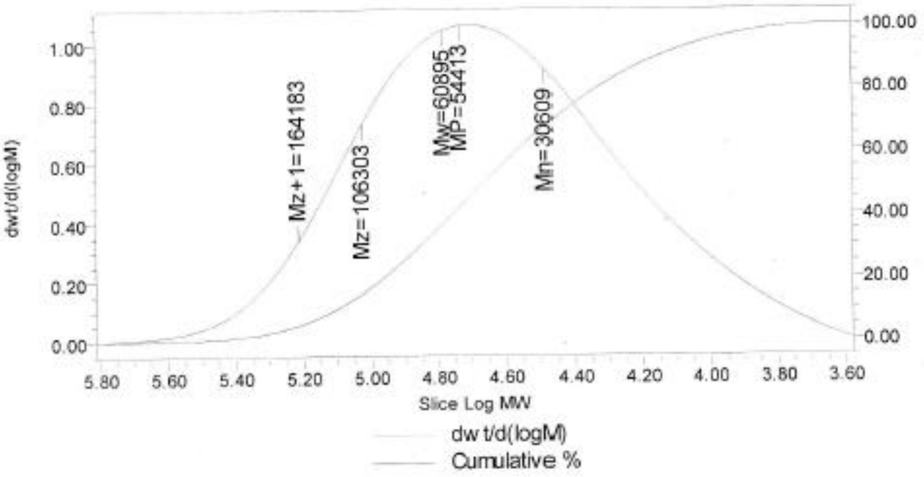
Gas permeation chromatograms of undegraded and heat-treated mcl-PHA

D.1 Gas permeation chromatogram of OA-derived PHA

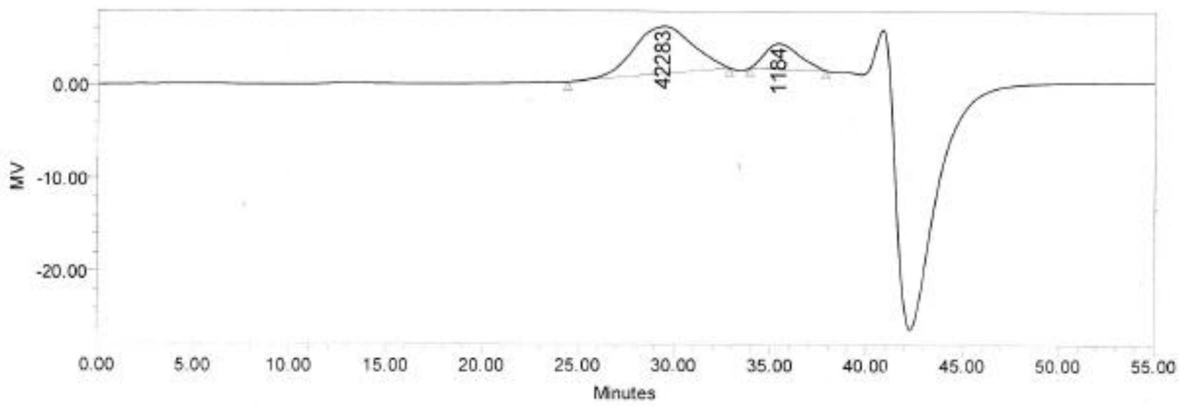


GPC Results

	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity
1	30609	60895	54413	106303	164183		1.989460
2							

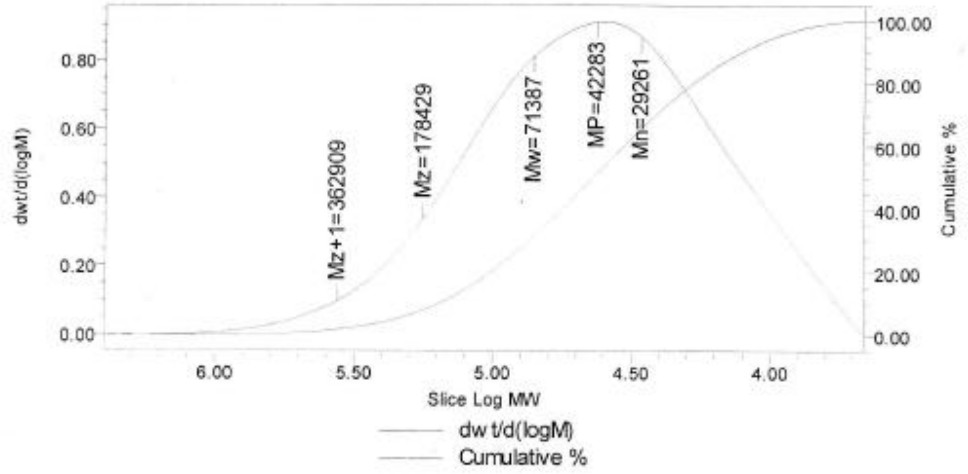


D.2 Gas permeation chromatogram of 160 ℃-treated OA-derived PHA

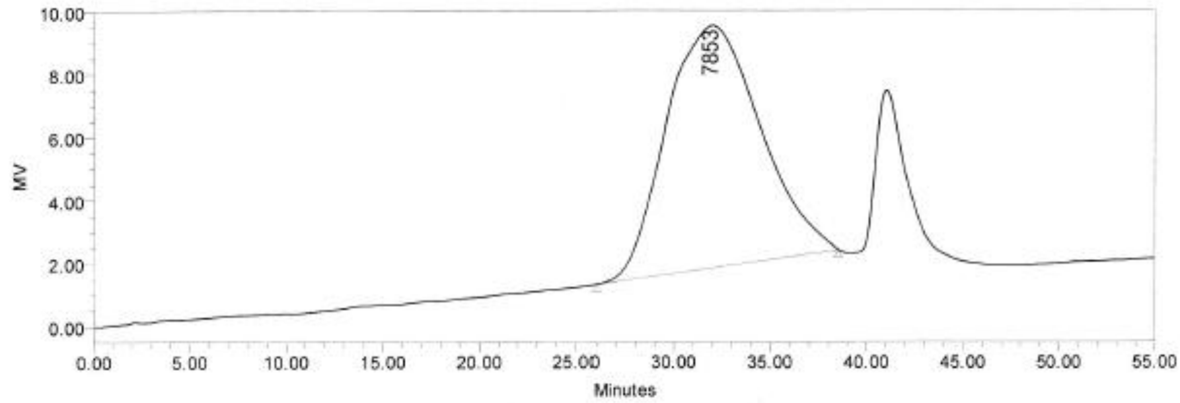


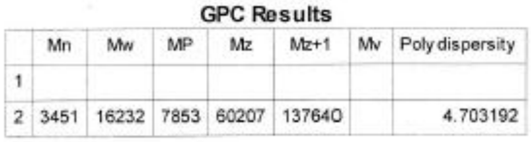
GPC Results

	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity
1	29261	71387	42283	178429	362909		2.439626
2	1001	1140	1184	1283	1421		1.138331



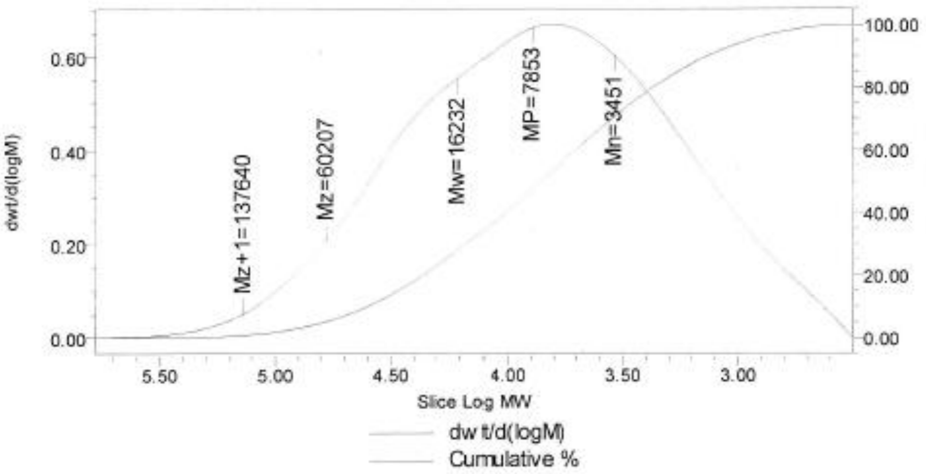
D.3 Gas permeation chromatogram of 170 ℃-treated OA-derived PHA



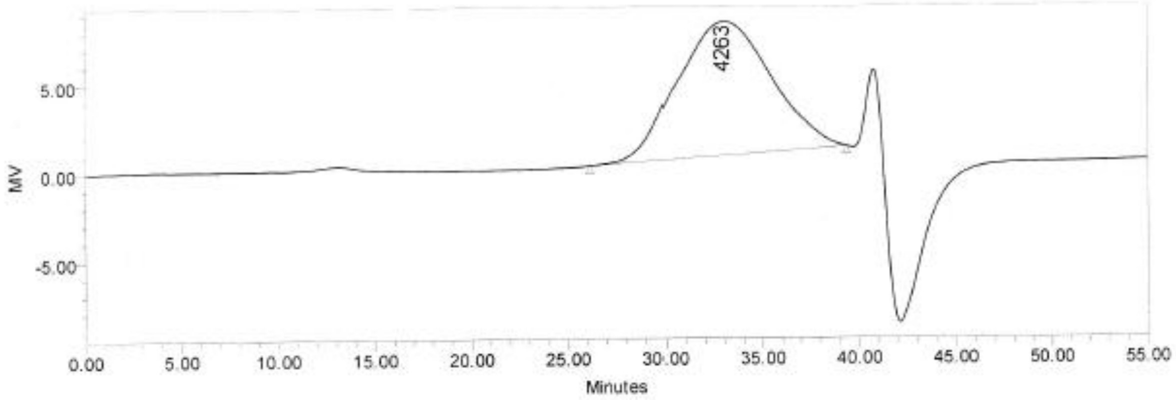


GPC Results

	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity
1							
2	3451	16232	7853	60207	137640		4.703192

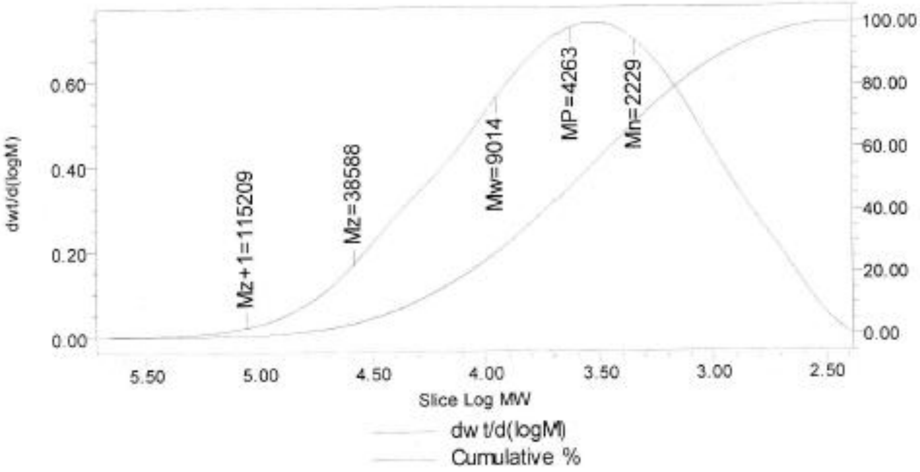


D.4 Gas permeation chromatogram of 180 ℃-treated OA-derived PHA

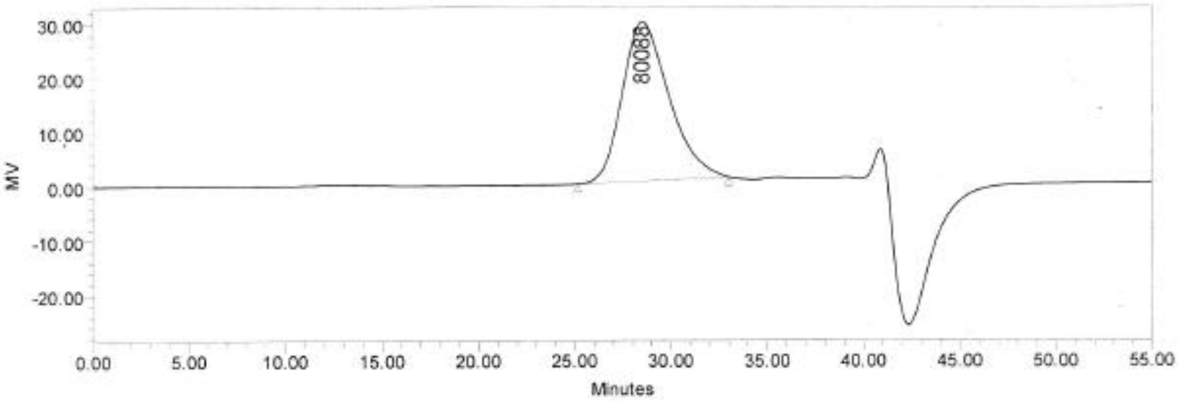


GPC Results

	Mn	Mw	MP	Mz	Mz+1	Mv	Polly dispersity
1							
2	2229	9014	4263	38588	115209		4.043439

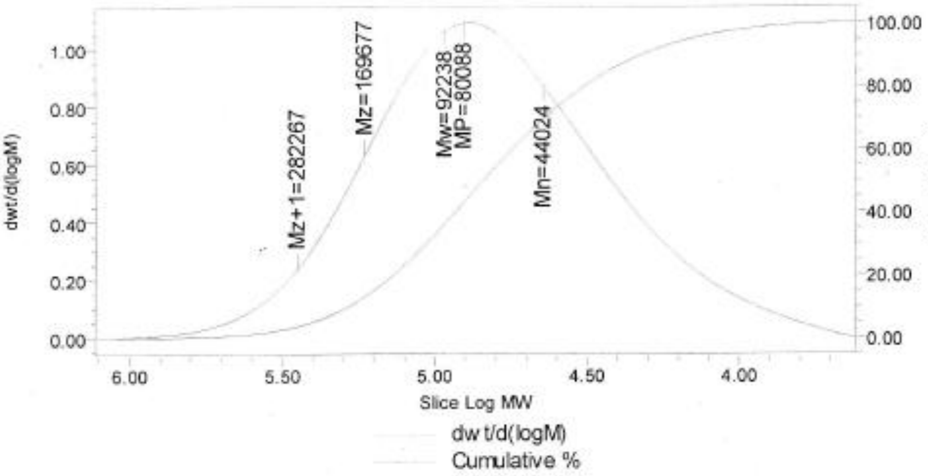


D.5 Gas permeation chromatogram of SPKO-derived PHA

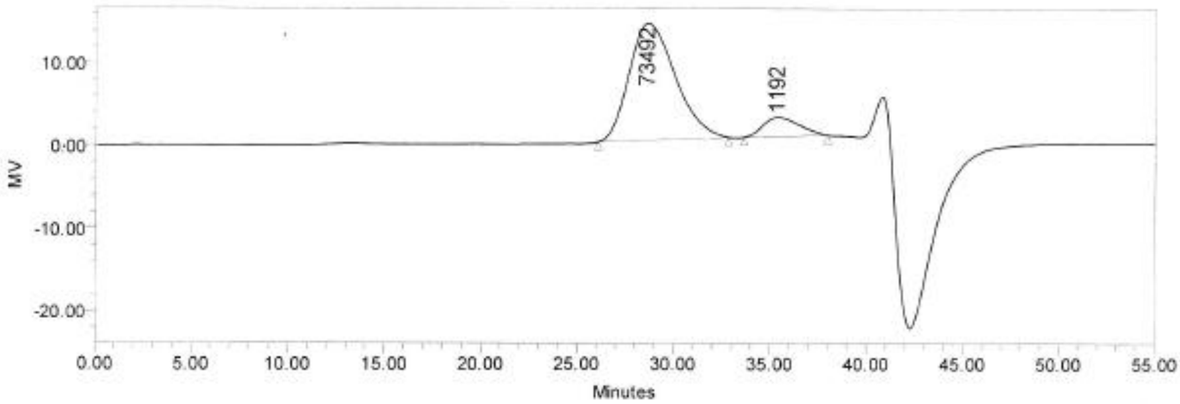


GPC Results

	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity
1	44024	92238	80088	169677	282267		2.095180
2							

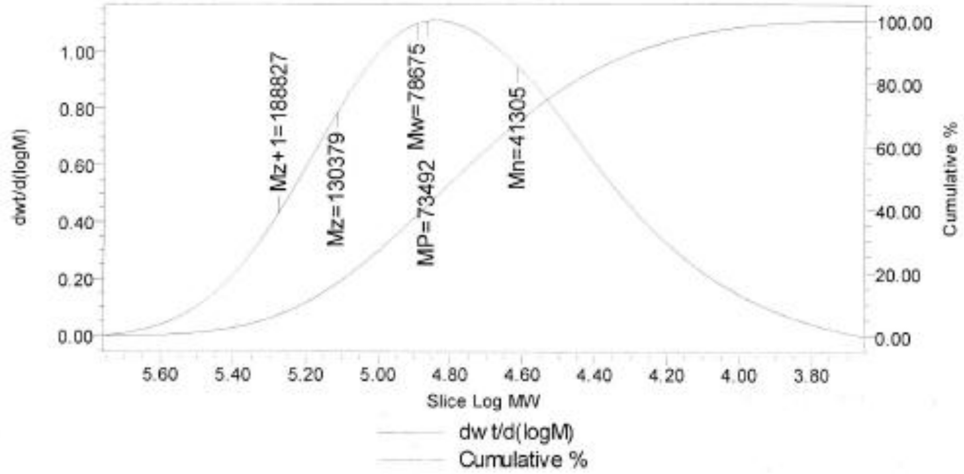


D.6 Gas permeation chromatogram of 160 ℃-treated SPKO-derived PHA

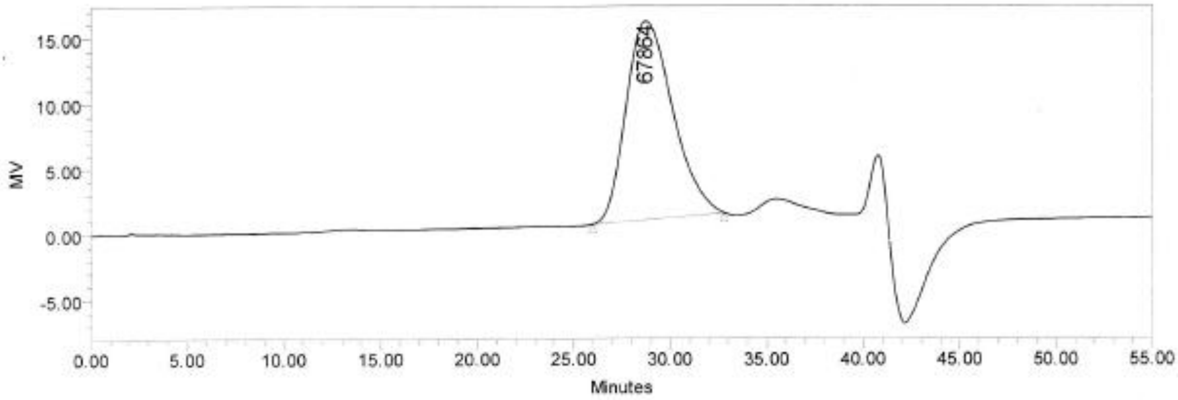


GPC Results

	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity
1	41305	78675	73492	130379	188827		1.904736
2	989	1144	1192	1309	1472		1.157389

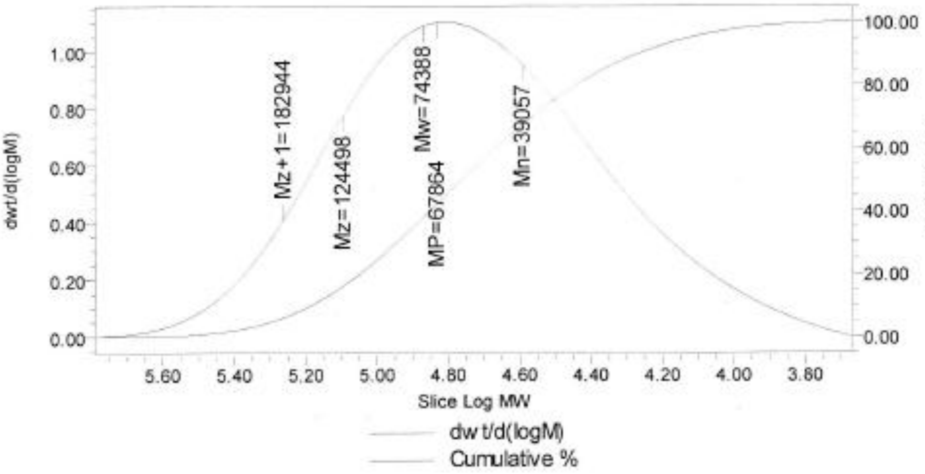


D.7 Gas permeation chromatogram of 170 ℃-treated SPKO-derived PHA

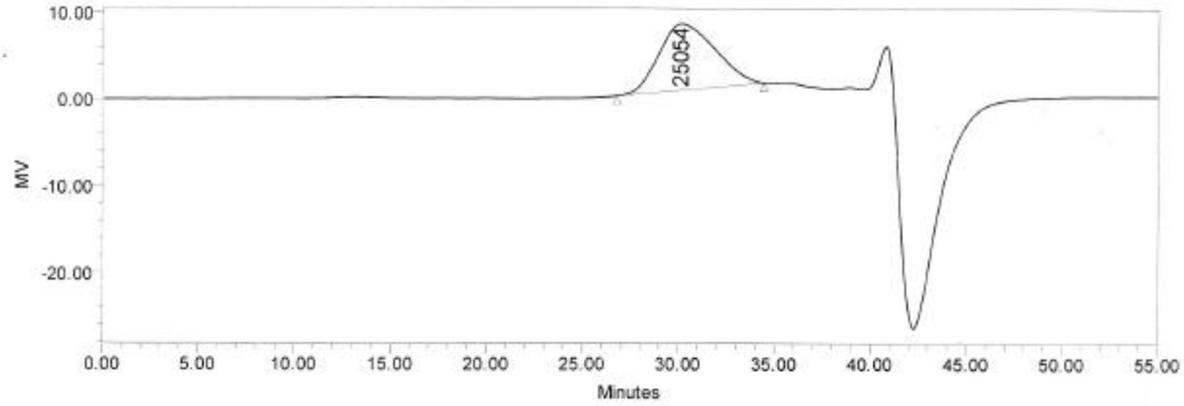


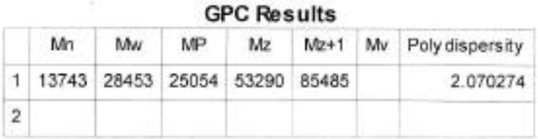
GPC Results

	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity
1	39057	74388	67864	124498	182944		1.904584
2							

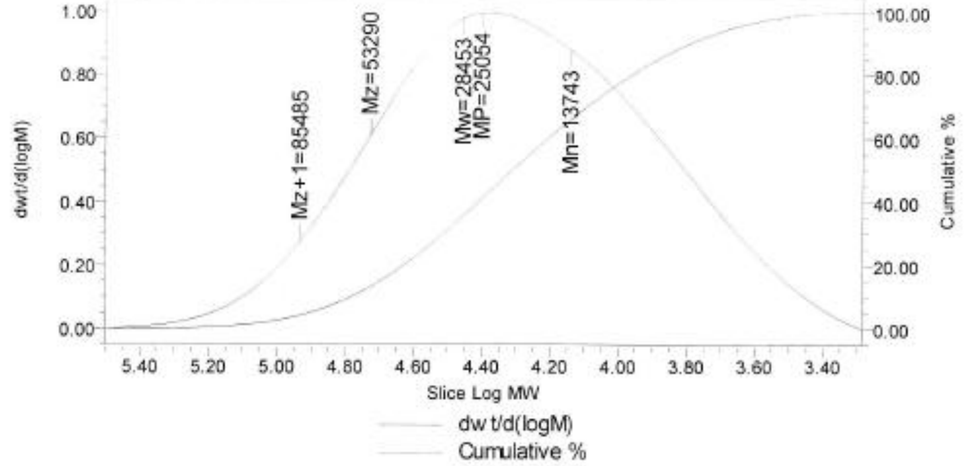


D.8 Gas permeation chromatogram of 180 ℃-treated SPKO-derived PHA

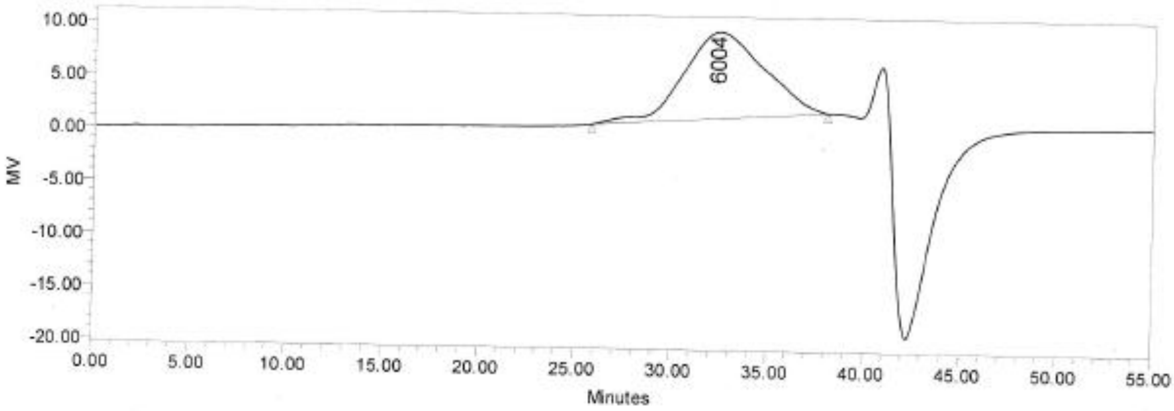



GPC Results

	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity
1	13743	28453	25054	53290	85485		2.070274
2							

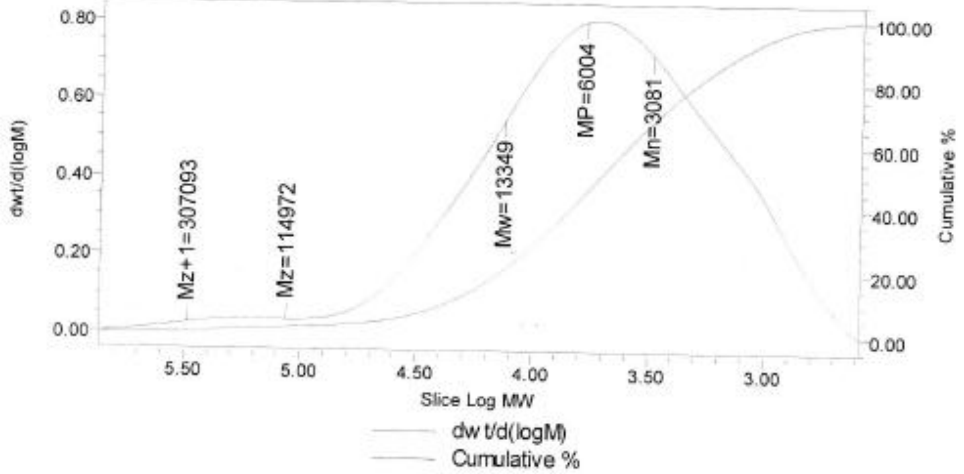


D.9 Gas permeation chromatogram of 190 ℃-treated SPKO-derived PHA



GPC Results

	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity
1							
2	3081	13349	6004	114972	307093		4.333209



APPENDIX E

Determinations of pH, acid dissociation constant (K_a), pK_a, degree of dissociation (α) and standard Gibbs free energy change ($\Delta G°$) of PHA degradation products

(i) Concentration of hydroxyalkanoic acids ≡ Concentration of -COOH terminals

(ii) Denoting hydroxyalkanoic acid as HA, hydrogen ions as H^+, conjugate base as A^-, concentration of HA as C and degree of dissociation as α

Dissociation of weak acid, HA in aqueous is shown in following equation:

$$
\begin{array}{rccc}
 & HA_{(aq)} \Leftrightarrow & H^+_{(aq)} + & A^-_{(aq)} \\
\text{Start:} & C & 0 & 0 \\
\text{Change:} & -\alpha C & +\alpha C & +\alpha C \\
\text{At equilibrium:} & C(1-\alpha) & \alpha C & \alpha C
\end{array}
$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \text{Equation (1)}$$

$$= \frac{(\alpha C)(\alpha C)}{C(1-\alpha)} \qquad \text{where } 0 < \alpha < 1$$

Since hydroxyalkanoic acid (HA) is a weak acid,

$\alpha <<<<< 1$

Thus, $K_a \approx \frac{(\alpha C)(\alpha C)}{C}$ and $pK_a = -\log_{10} K_a$

(iii) α can be determined from the two equations as followed:

$$\alpha = \sqrt{Ka/C} \qquad \text{Equation (2)}$$

or

$$\alpha = [H^+]/[HA] \qquad \text{Equation (3)}$$

(iv) $\Delta G°$, change in standard Gibbs free energy of the process can be calculated from the following relationship:

$$\Delta G° = RT\ 2.303\ pK_a$$

where $T = (95+273)$ K = 368 K

$R = 8.3143$ J K^{-1} mol^{-1}

E.1 Calculations of pH, K_a, pK_a, α and $G°$ for 180 ℃-treated SPKO-derived PHA degradation products

Replicate 1:

pH of control boiled distilled water (95 ℃) = 5.81

$$\text{pH of } dH_2O = 5.81$$

$$[H^+] \text{ from dissociation of water} = 10^{-5.81}$$

$$= 1.55\text{x}10^{-6} \text{ mol dm}^{-3}$$

pH of 180 ℃-treated PHA_{SPKO} degradation products in boiled distilled water = 5.64

$$\text{pH of } HA_{(aq)} = 5.64$$

$$[H^+] \text{ from dissociations of HA and water} = 10^{-5.64}$$

$$= 2.29\text{x}10^{-6} \text{ mol dm}^{-3}$$

Therefore, $[H^+]$ from dissociation of HA = $(2.29\text{x}10^{-6} - 1.55\text{x}10^{-6})$ mol dm^{-3}

$$= 7.4\text{x}10^{-7} \text{ mol dm}^{-3}$$

$$\text{pH of HA} = -\log_{10}(7.4\text{x}10^{-7} \text{ mol dm}^{-3})$$

$$= 6.13$$

Concentration of –COOH terminal from end group analysis = [HA]

$$= 2.22 \text{ x } 10^{-4} \text{ mol g}^{-1}$$

$$= 2.22\text{x}10^{-1} \text{ mol dm}^{-3}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{(7.4\text{x}10^{-7})^2 \text{ mol}^2 \text{ dm}^{-6}}{2.22\text{x}10^{-1} \text{ mol dm}^{-3}}$$

$$K_a = 2.47\text{x}10^{-12} \text{ mol dm}^{-3}$$

Since

$$pK_a = -\log_{10} K_a$$

$$= -\log_{10}(2.47\text{x}10^{-12})$$

$$= 11.61$$

$$\alpha = \sqrt{Ka/C} \text{ --------------------Equation (2)}$$

$$= \sqrt{(2.47x10^{-12})/0.222}$$

$$= 3.3\text{x}10^{-6}$$

$$\alpha = [H^+]/[HA] \text{ ---------------Equation (3)}$$

$$= (7.4\text{x}10^{-7})/0.222$$

$$= 3.3\text{x}10^{-6}$$

Both equations (2) and (3) produce the similar α value of $3.3\text{x}10^{-6}$.

$$\Delta G° = RT\ 2.303\ pK_a$$

$$= (8.3143 \cdot 368 \cdot 2.303 \cdot 11.61) \text{ J mol}^{-1}$$

$$= 81.8 \text{ x } 10^3 \text{ J mol}^{-1}$$

$$= 81.8 \text{ kJ mol}^{-1}$$

Replicate 2:

pH of control boiled distilled water (95 °C) = 5.90

pH of dH_2O = 5.90

$[H^+]$ from dissociation of water = $10^{-5.90}$

= $1.26\text{x}10^{-6}$ mol dm^{-3}

pH of 180 °C-treated PHA_{SPKO} degradation products in boiled distilled water = 5.77

pH of $HA_{(aq)}$ = 5.77

$[H^+]$ from dissociations of HA and water = $10^{-5.77}$

= $1.70\text{x}10^{-6}$ mol dm^{-3}

Therefore, $[H^+]$ from dissociation of HA = ($1.70\text{x}10^{-6}$ -$1.26\text{x}10^{-6}$) mol dm^{-3}

= $4.4\text{x}10^{-7}$ mol dm^{-3}

pH of HA = -$\log_{10}$ ($4.4\text{x}10^{-7}$ mol dm^{-3})

= 6.36

Concentration of –COOH terminal from end group analysis = [HA]

= 2.22 x 10^{-4} mol g^{-1}

=$2.22\text{x}10^{-1}$ mol dm^{-3}

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{(4.4\text{x}10^{-7})^2 \text{ mol}^2 \text{ dm}^{-6}}{2.22\text{x}10^{-1} \text{ mol dm}^{-3}}$$

K_a = $8.72\text{x}10^{-13}$ mol dm^{-3}

Since

$pK_a = -\log_{10} K_a$

$= -\log_{10} (8.72\text{x}10^{-13})$

$= 12.06$

$\alpha = \sqrt{Ka/C}$ --------------------Equation (2)

$= \sqrt{(8.72x10^{-13})/0.222}$

= $1.98\text{x}10^{-6}$

$\alpha = [H^+]/[HA]$ ---------------Equation (3)

= $(4.4\text{x}10^{-7})/0.222$

= $1.98\text{x}10^{-6}$

Both equations (2) and (3) produce the similar α value of $1.98\text{x}10^{-6}$.

$\Delta G° = RT\ 2.303\ pK_a$

= (8.3143 ·368 ·2.303 ·12.06) J mol^{-1}

= 85.0 x 10^3 J mol^{-1}

= 85.0 kJ mol^{-1}

Therefore, the average values of pH, K_a, pK_a, α and $G°$ for 180 °C-treated SPKO-derived PHA degradation products are as following:

pH : 6.3 ± 0.2
K_a : 1.7 x 10^{-12} mol dm^{-3}
pK_a : 11.8 ± 0.3
α : 2.6 x 10^{-6}
$\Delta G°$: 83.4 ± 2.2 kJ mol^{-1}

E.2 Calculations of pH, K_a, pK_a, α and $G°$ for 190 ℃-treated SPKO-derived PHA degradation products

Replicate 1:

pH of control boiled distilled water (95 ℃) = 5.82

pH of dH_2O = 5.82

$[H^+]$ from dissociation of water = $10^{-5.82}$

= $1.52\text{x}10^{-6}$ mol dm^{-3}

pH of 190 ℃-treated PHA_{SPKO} degradation products in boiled distilled water = 4.74

pH of $HA_{(aq)}$ = 4.74

$[H^+]$ from dissociations of HA and water = $10^{-4.74}$

= $1.82\text{x}10^{-5}$ mol dm^{-3}

Therefore, $[H^+]$ from dissociation of HA = $(1.82\text{x}10^{-5} - 1.52\text{x}10^{-6})$ mol dm^{-3}

= $1.67\text{x}10^{-5}$ mol dm^{-3}

pH of HA = $-\log_{10}(1.67\text{x}10^{-5}$ mol dm$^{-3})$

= 4.78

Concentration of –COOH terminal from end group analysis = [HA]

= $6.29 \text{ x } 10^{-4}$ mol g^{-1}

= $6.29\text{x}10^{-1}$ mol dm^{-3}

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{(1.67\text{x}10^{-5})^2 \text{ mol}^2 \text{ dm}^{-6}}{6.29\text{x}10^{-1} \text{ mol dm}^{-3}}$$

$K_a = 4.42\text{x}10^{-10}$ mol dm^{-3}

Since

$pK_a = -\log_{10} K_a$

$= -\log_{10}(4.42\text{x}10^{-10})$

$= 9.35$

$\alpha = \sqrt{Ka/C}$ --------------------Equation (2)

$= \sqrt{(4.42x10^{-10})/0.629}$

$= 2.65\text{x}10^{-5}$

$\alpha = [H^+]/[HA]$ ---------------Equation (3)

$= (1.67\text{x}10^{-5})/0.629$

$= 2.65\text{x}10^{-5}$

Both equations (2) and (3) produce the similar α value of $2.65\text{x}10^{-5}$.

$\Delta G° = RT\ 2.303\ pK_a$

$= (8.3143 \cdot 368 \cdot 2.303 \cdot 9.35)$ J mol^{-1}

$= 65.9 \text{ x } 10^3$ J mol^{-1}

$= 65.9$ kJ mol^{-1}

Replicate 2:

pH of control boiled distilled water (95 ℃) = 5.80

pH of dH_2O = 5.80

$[H^+]$ from dissociation of water = $10^{-5.80}$

= $1.58\text{x}10^{-6}$ mol dm^{-3}

pH of 190 ℃-treated PHA_{SPKO} degradation products in boiled distilled water = 4.72

pH of $HA_{(aq)}$ = 4.72

$[H^+]$ from dissociations of HA and water = $10^{-4.72}$

= $1.91\text{x}10^{-5}$ mol dm^{-3}

Therefore, $[H^+]$ from dissociation of HA = ($1.91\text{x}10^{-5}$ -$1.58\text{x}10^{-6}$) mol dm^{-3}

= $1.75\text{x}10^{-5}$ mol dm^{-3}

pH of HA =-$\log_{10}$ ($1.75\text{x}10^{-5}$ mol dm^{-3})

= 4.76

Concentration of –COOH terminal from end group analysis = [HA]

= 6.29 x 10^{-4} mol g^{-1}

= $6.29\text{x}10^{-1}$ mol dm^{-3}

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{(1.75\text{x}10^{-5})^2 \text{ mol}^2 \text{ dm}^{-6}}{6.29\text{x}10^{-1} \text{ mol dm}^{-3}}$$

K_a = $4.88\text{x}10^{-10}$ mol dm^{-3}

Since

$pK_a = -\log_{10} K_a$

$= -\log_{10} (4.88\text{x}10^{-10})$

= 9.31

$\alpha = \sqrt{Ka/C}$ --------------------Equation (2)

$= \sqrt{(4.88x10^{-10})/0.629}$

= $2.79\text{x}10^{-5}$

$\alpha = [H^+]/[HA]$ ---------------Equation (3)

= ($1.75\text{x}10^{-5}$)/0.629

= $2.79\text{x}10^{-5}$

Both equations (2) and (3) produce the similar α value of $2.79\text{x}10^{-5}$.

$\Delta G° = RT\ 2.303\ pK_a$

= (8.3143 ·368 ·2.303 ·9.31) J mol^{-1}

= 65.6 x 10^3 J mol^{-1}

= 65.6 kJ mol^{-1}

Therefore, the average values of pH, K_a, pK_a, α and $G°$ for 190 ℃-treated SPKO-derived PHA degradation products are as following:

pH : 4.8 ± 0.01
K_a : 4.7 x 10^{-10} mol dm^{-3}
pK_a : 9.3 ± 0.03
α : 2.7 x 10^{-5}
$\Delta G°$: 65.8 ± 0.1 kJ mol^{-1}

E.3 Calculations of pH, K_a, pK_a, α and $G°$ for 170 °C-treated OA-derived PHA degradation products

Replicate 1:

pH of control boiled distilled water (95 °C) = 5.51

pH of dH_2O = 5.51

$[H^+]$ from dissociation of water = $10^{-5.51}$

$= 3.09\text{x}10^{-6}$ mol dm^{-3}

pH of 170 °C-treated PHA_{OA} degradation products in boiled distilled water =5.36

pH of $HA_{(aq)}$ = 5.36

$[H^+]$ from dissociations of HA and water = $10^{-5.36}$

$= 4.37\text{x}10^{-6}$ mol dm^{-3}

Therefore, $[H^+]$ from dissociation of HA = $(4.37\text{x}10^{-6} - 3.09\text{x}10^{-6})$ mol dm^{-3}

$= 1.28\text{x}10^{-6}$ mol dm^{-3}

pH of HA = $-\log_{10}(1.28\text{x}10^{-6}$ mol $dm^{-3})$

= 5.89

Concentration of –COOH terminal from end group analysis = [HA]

$= 2.60 \text{ x } 10^{-4}$ mol g^{-1}

$=2.60\text{x}10^{-1}$ mol dm^{-3}

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{(1.28\text{x}10^{-6})^2 \text{ mol}^2 \text{ dm}^{-6}}{2.60\text{x}10^{-1} \text{ mol dm}^{-3}}$$

$K_a = 6.30\text{x}10^{-12}$ mol dm^{-3}

Since

$pK_a = -\log_{10} K_a$

$= -\log_{10}(6.30\text{x}10^{-12})$

$= 11.20$

$\alpha = \sqrt{Ka/C}$ --------------------Equation (2)

$= \sqrt{(6.3x10^{-12})/0.26}$

$= 4.92\text{x}10^{-6}$

$\alpha = [H^+]/[HA]$ ---------------Equation (3)

$= (1.28\text{x}10^{-6})/0.260$

$= 4.92\text{x}10^{-6}$

Both equations (2) and (3) produce the similar α value of $4.92\text{x}10^{-6}$.

$\Delta G° = RT\ 2.303\ pK_a$

$= (8.3143 \cdot 368 \cdot 2.303 \cdot 11.20)$ J mol^{-1}

$= 78.9 \text{ x } 10^3$ J mol^{-1}

$= 78.9$ kJ mol^{-1}

Replicate 2:

pH of control boiled distilled water (95 ℃) = 5.85

pH of dH_2O = 5.85

$[H^+]$ from dissociation of water = $10^{-5.85}$

= $1.41\text{x}10^{-6}$ mol dm^{-3}

pH of 170 ℃-treated PHA_{OA} degradation products in boiled distilled water = 5.67

pH of $HA_{(aq)}$ = 5.67

$[H^+]$ from dissociations of HA and water = $10^{-5.67}$

= $2.14\text{x}10^{-6}$ mol dm^{-3}

Therefore, $[H^+]$ from dissociation of HA = ($2.14\text{x}10^{-6}$ -$1.41\text{x}10^{-6}$) mol dm^{-3}

= $7.3\text{x}10^{-7}$ mol dm^{-3}

pH of HA = $-\log_{10}$ ($7.3\text{x}10^{-7}$ mol dm^{-3})

= 6.14

Concentration of –COOH terminal from end group analysis = [HA]

= 2.60 x 10^{-4} mol g^{-1}

=$2.60\text{x}10^{-1}$ mol dm^{-3}

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{(7.3\text{x}10^{-7})^2 \text{ mol}^2 \text{ dm}^{-6}}{2.60\text{x}10^{-1} \text{ mol dm}^{-3}}$$

K_a = $2.05\text{x}10^{-12}$ mol dm^{-3}

Since

$pK_a = -\log_{10} K_a$

$= -\log_{10} (2.05\text{x}10^{-12})$

$= 11.69$

$\alpha = \sqrt{Ka/C}$ --------------------Equation (2)

$=\sqrt{(2.05x10^{-12})/0.26}$

$= 2.81\text{x}10^{-6}$

$\alpha = [H^+]/[HA]$ ---------------Equation (3)

$= (7.3\text{x}10^{-7})/0.26$

$= 2.81\text{x}10^{-6}$

Both equations (2) and (3) produce the similar α value of $2.81\text{x}10^{-6}$.

$\Delta G° = RT\ 2.303\ pK_a$

$= (8.3143 \cdot 368 \cdot 2.303 \cdot 11.69)$ J mol^{-1}

$= 82.4 \text{ x } 10^3$ J mol^{-1}

$= 82.4$ kJ mol^{-1}

Therefore, the average values of pH, K_a, pK_a, α and $G°$ for 170 ℃-treated OA-derived PHA degradation products are as following:

pH : 6.0 ± 0.2
K_a : 4.2 x 10^{-12} mol dm^{-3}
pK_a : 11.5 ± 0.3
α : 3.9 x 10^{-6}
$\Delta G°$: 80.7 ± 2.4 kJ mol^{-1}

E.4 Calculations of pH, K_a, pK_a, α and $G°$ for 180 ℃-treated OA-derived PHA degradation products

Replicate 1:

pH of control boiled distilled water (95 ℃) = 5.80

pH of dH_2O = 5.80

$[H^+]$ from dissociation of water = $10^{-5.80}$

= $1.58\text{x}10^{-6}$ mol dm^{-3}

pH of 180 ℃-treated PHA_{OA} degradation products in boiled distilled water = 4.99

pH of $HA_{(aq)}$ = 4.99

$[H^+]$ from dissociations of HA and water = $10^{-4.99}$

= $1.02\text{x}10^{-5}$ mol dm^{-3}

Therefore, $[H^+]$ from dissociation of HA = ($1.02\text{x}10^{-5}$ -$1.58\text{x}10^{-6}$) mol dm^{-3}

= $8.62\text{x}10^{-6}$ mol dm^{-3}

pH of HA = $-\log_{10}$ ($8.62\text{x}10^{-6}$ mol dm^{-3})

= 5.06

Concentration of –COOH terminal from end group analysis = [HA]

= $5.91 \text{ x } 10^{-4}$ mol g^{-1}

= $5.91\text{x}10^{-1}$ mol dm^{-3}

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{(8.62\text{x}10^{-6})^2 \text{ mol}^2 \text{ dm}^{-6}}{5.91\text{x}10^{-1} \text{ mol dm}^{-3}}$$

K_a = $1.26\text{x}10^{-10}$ mol dm^{-3}

Since

$pK_a = -\log_{10} K_a$

$= -\log_{10} (1.26\text{x}10^{-10})$

= 9.90

$\alpha = \sqrt{Ka/C}$ --------------------Equation (2)

$= \sqrt{(1.26x10^{-10})/0.591}$

= $1.46\text{x}10^{-5}$

$\alpha = [H^+]/[HA]$ ---------------Equation (3)

= $(8.62\text{x}10^{-6})/0.591$

= $1.46\text{x}10^{-5}$

Both equations (2) and (3) produce the similar α value of $1.46\text{x}10^{-5}$.

$\Delta G° = RT \, 2.303 \, pK_a$

= (8.3143 ·368 ·2.303 ·9.90) J mol^{-1}

= $69.8 \text{ x } 10^3$ J mol^{-1}

= 69.8 kJ mol^{-1}

Replicate 2:

pH of control boiled distilled water (95 ℃) = 5.79

pH of dH_2O = 5.79

$[H^+]$ from dissociation of water = $10^{-5.79}$

$= 1.62\text{x}10^{-6}$ mol dm^{-3}

pH of 180 ℃-treated PHA_{OA} degradation products in boiled distilled water = 4.98

pH of $HA_{(aq)}$ = 4.98

$[H^+]$ from dissociations of HA and water = $10^{-4.98}$

$= 1.05\text{x}10^{-5}$ mol dm^{-3}

Therefore, $[H^+]$ from dissociation of HA = $(1.05\text{x}10^{-5} - 1.62\text{x}10^{-6})$ mol dm^{-3}

$= 8.88\text{x}10^{-6}$ mol dm^{-3}

pH of HA = $-\log_{10}(8.88\text{x}10^{-6}$ mol dm$^{-3})$

= 5.05

Concentration of –COOH terminal from end group analysis = [HA]

$= 5.91 \text{ x } 10^{-4}$ mol g^{-1}

$= 5.91 \text{ x}10^{-1}$ mol dm^{-3}

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{(8.88\text{x}10^{-6})^2 \text{ mol}^2 \text{ dm}^{-6}}{5.91\text{x}10^{-1} \text{ mol dm}^{-3}}$$

$K_a = 1.33\text{x}10^{-10}$ mol dm^{-3}

Since

$pK_a = -\log_{10} K_a$

$= -\log_{10}(1.33\text{x}10^{-10})$

$= 9.88$

$\alpha = \sqrt{Ka/C}$ --------------------Equation (2)

$= \sqrt{(1.33x10^{-10})/0.591}$

$= 1.50\text{x}10^{-5}$

$\alpha = [H^+]/[HA]$ ---------------Equation (3)

$= (8.88\text{x}10^{-6})/0.591$

$= 1.50\text{x}10^{-5}$

Both equations (2) and (3) produce the similar α value of 1.50 swswwx10^{-5}.

$\Delta G° = RT\ 2.303\ pK_a$

$= (8.3143 \cdot 368 \cdot 2.303 \cdot 9.88)$ J mol^{-1}

$= 69.6 \text{ x } 10^3$ J mol^{-1}

$= 69.6$ kJ mol^{-1}

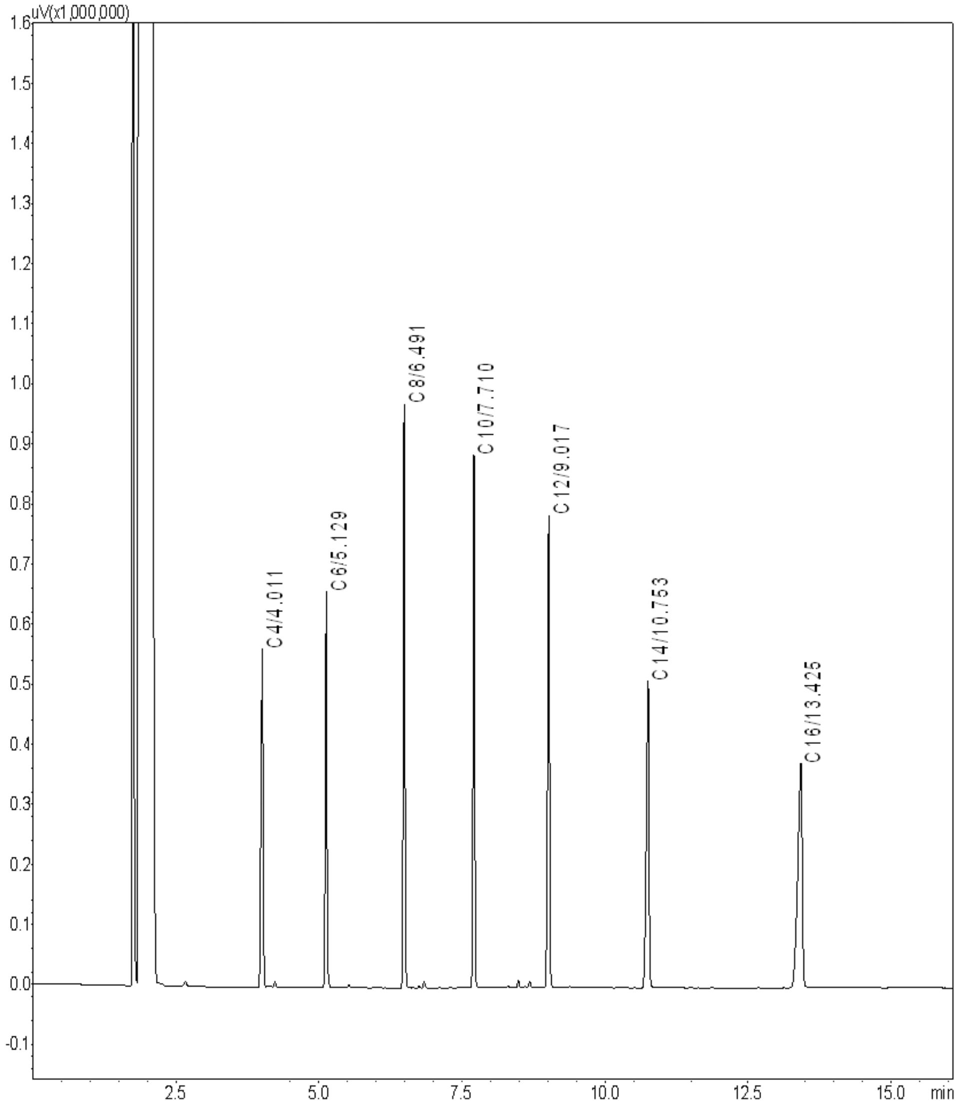
Therefore, the average values of pH, K_a, pK_a, α and $G°$ for 180 ℃-treated OA-derived PHA degradation products are as following:

pH : 5.1 ± 0.007
K_a : $1.3 \text{ x } 10^{-10}$ mol dm^{-3}
pK_a : 9.9 ± 0.01
α : $1.5 \text{ x } 10^{-5}$
$\Delta G°$: 69.7 ± 0.1 kJ mol^{-1}

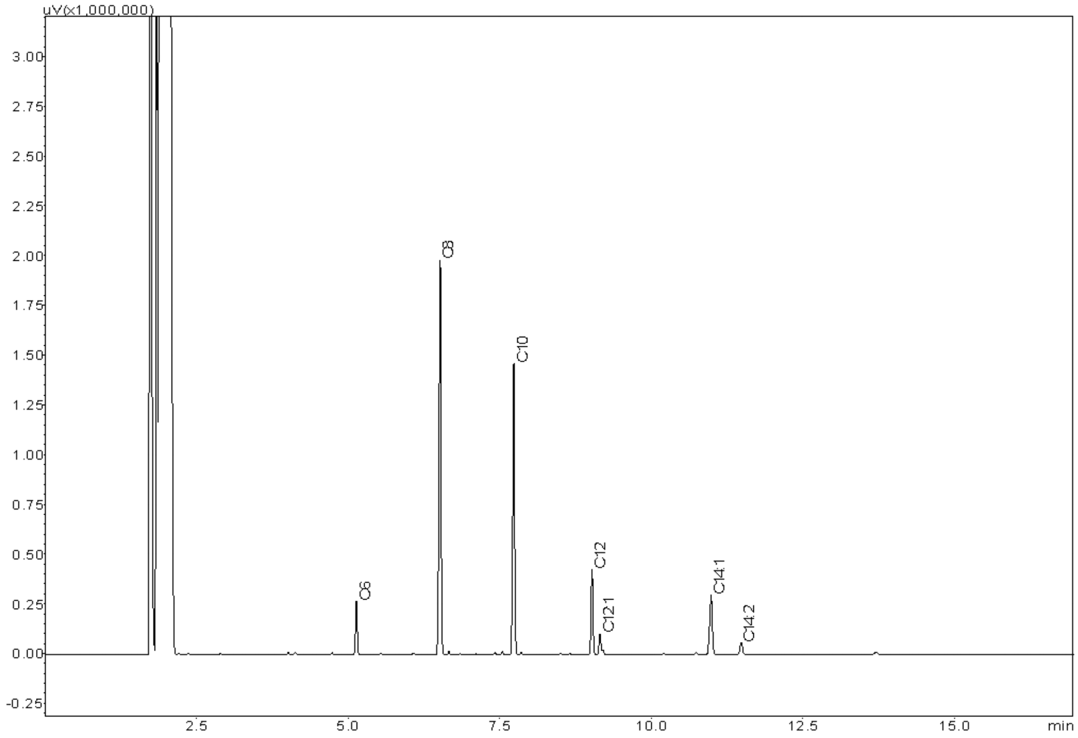
APPENDIX F:

Gas chromatograms of undegraded and heat-treated mcl-PHA

F.1 Gas chromatogram of the methyl esters standard

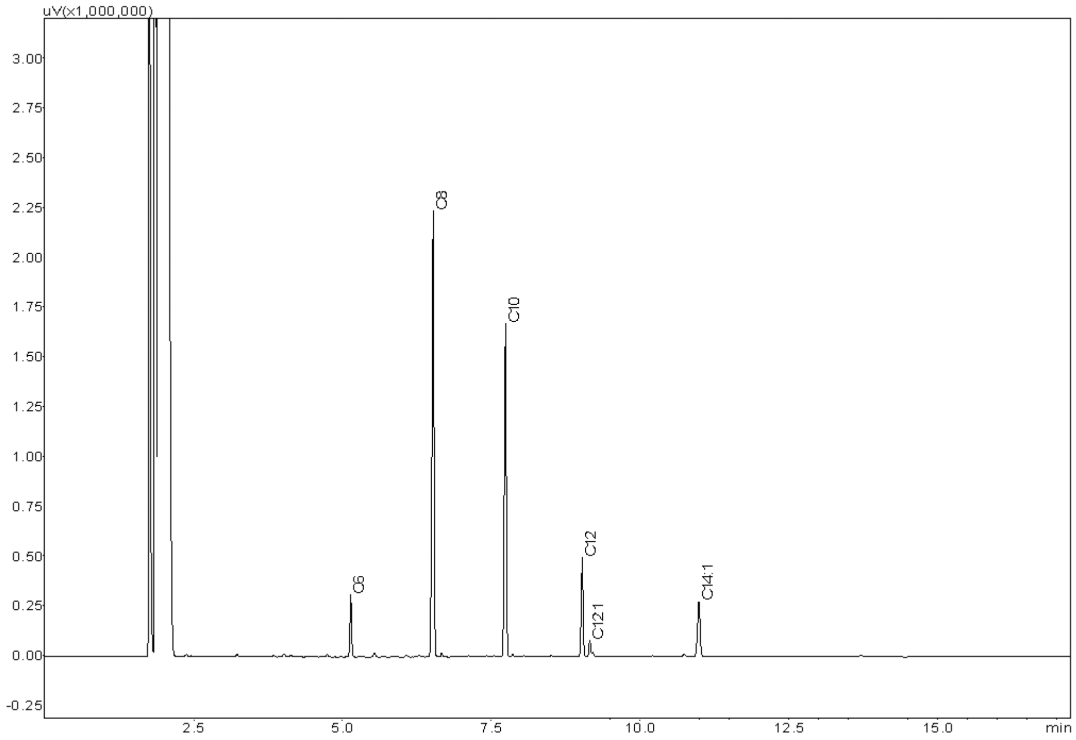


F.2 Gas chromatogram of OA-derived PHA



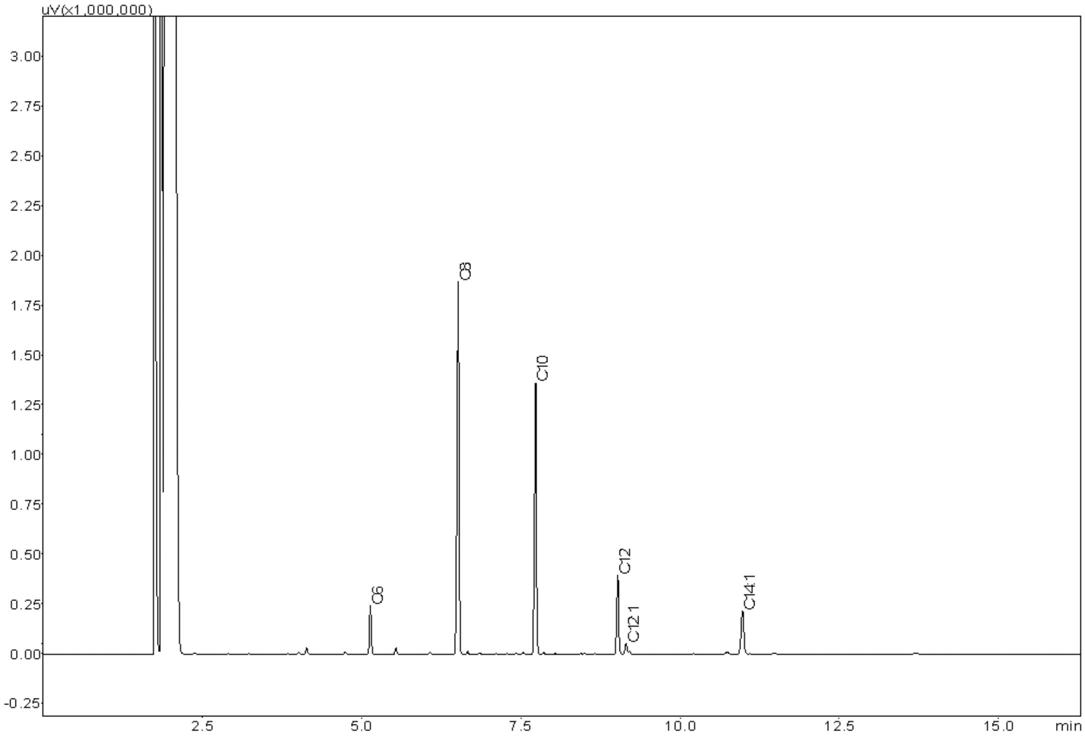
Retention Time (min)	Composition (wt %)	Compound ID	Monomer Name
5.14	4.96	C_6	3-hydroxyhexanoic acid
6.52	42.28	C_8	3-hydroxyoctanoic acid
7.73	29.99	C_{10}	3-hydroxydecanoic acid
9.02	9.13	C_{12}	3-hydroxydodecanoic acid
9.16	2.57	$C_{12:1}$	3-hydroxydodecenoic acid
10.99	9.15	$C_{14:1}$	3-hydroxytetradecenoic acid
11.49	1.92	$C_{14:2}$	3-hydroxytetradecadienoic acid

F.3 Gas chromatogram of 160 ℃-treated OA-derived PHA



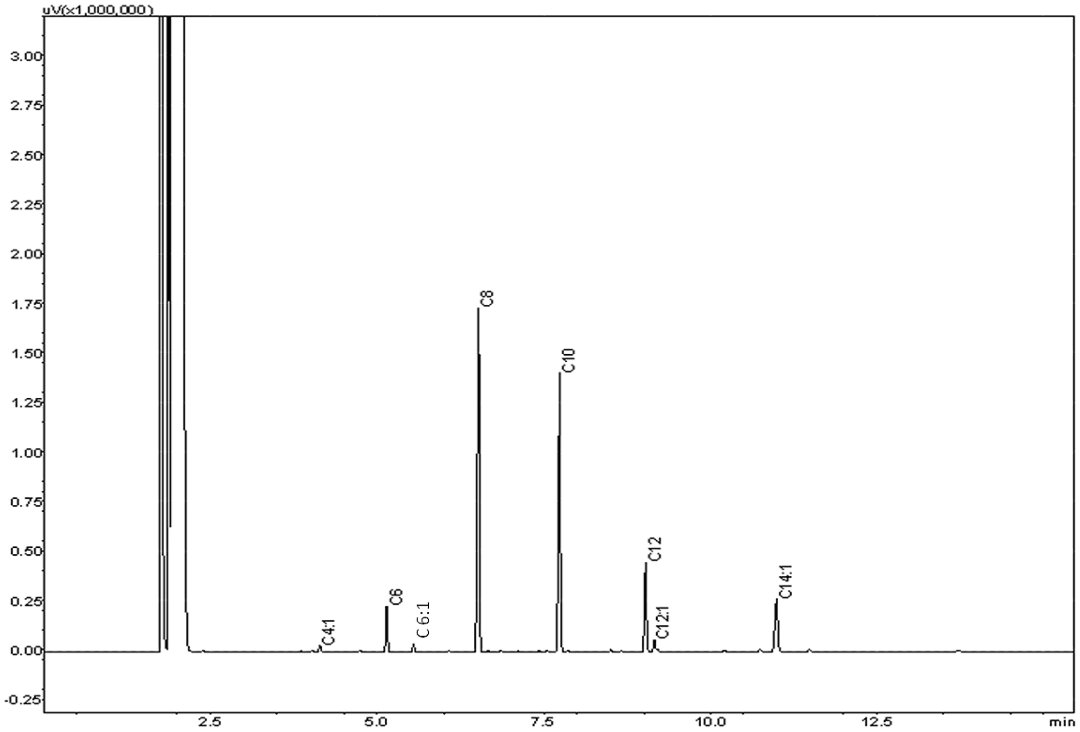
Retention Time (min)	Composition (wt %)	Compound ID	Monomer Name
5.14	5.27	C_6	3-hydroxyhexanoic acid
6.52	44.49	C_8	3-hydroxyoctanoic acid
7.74	31.52	C_{10}	3-hydroxydecanoic acid
9.03	9.61	C_{12}	3-hydroxydodecanoic acid
9.16	1.69	$C_{12:1}$	3-hydroxydodecenoic acid
10.99	7.42	$C_{14:1}$	3-hydroxytetradecenoic acid

F.4 Gas chromatogram of 170 ℃-treated OA-derived PHA



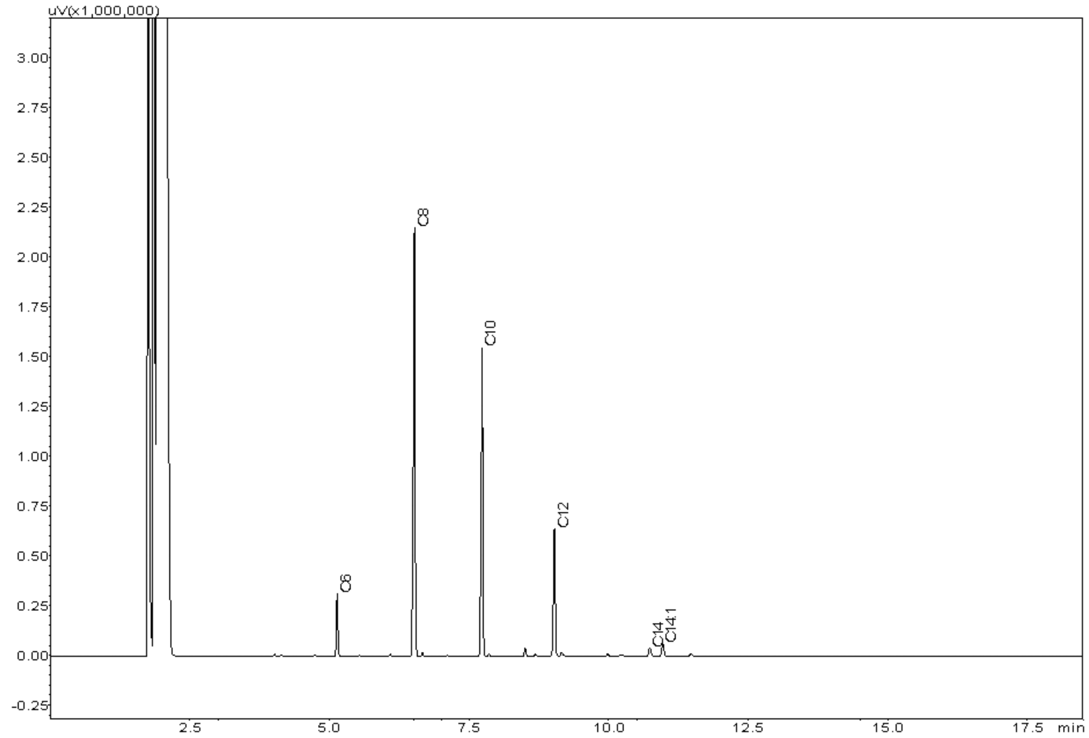
Retention Time (min)	Composition (wt %)	Compound ID	Monomer Name
5.14	5.28	C_6	3-hydroxyhexanoic acid
6.52	44.60	C_8	3-hydroxyoctanoic acid
7.74	31.63	C_{10}	3-hydroxydecanoic acid
9.02	9.62	C_{12}	3-hydroxydodecanoic acid
9.16	1.40	$C_{12:1}$	3-hydroxydodecenoic acid
10.99	7.47	$C_{14:1}$	3-hydroxytetradecenoic acid

F.5 Gas chromatogram of 180 ℃-treated OA-derived PHA



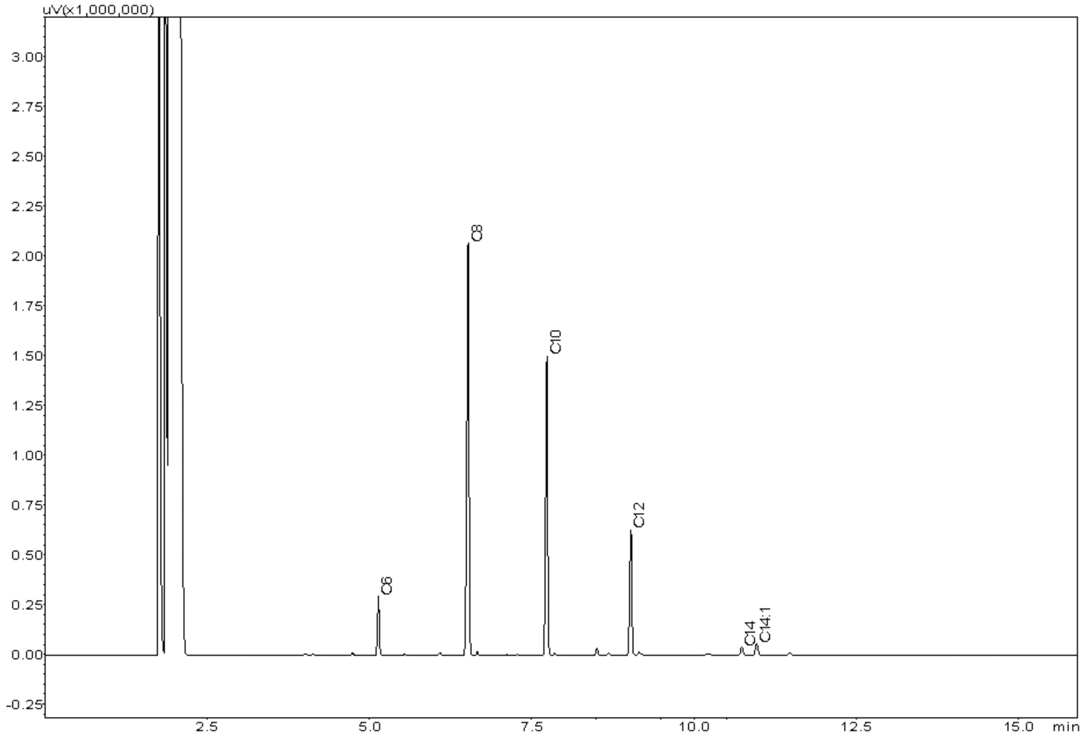
Retention Time (min)	Composition (wt %)	Compound ID	Monomer Name
4.14	0.99	$C_{4:1}$	3-hydroxybutenoic acid
5.14	4.97	C_6	3-hydroxyhexanoic acid
5.54	0.99	$C_{6:1}$	3-hydroxyhexenoic acid
6.52	39.62	C_8	3-hydroxyoctanoic acid
7.74	31.76	C_{10}	3-hydroxydecanoic acid
9.03	10.95	C_{12}	3-hydroxydodecanoic acid
9.16	1.59	$C_{12:1}$	3-hydroxydodecenoic acid
10.99	9.13	$C_{14:1}$	3-hydroxytetradecenoic acid

F.6 Gas chromatogram of SPKO-derived PHA



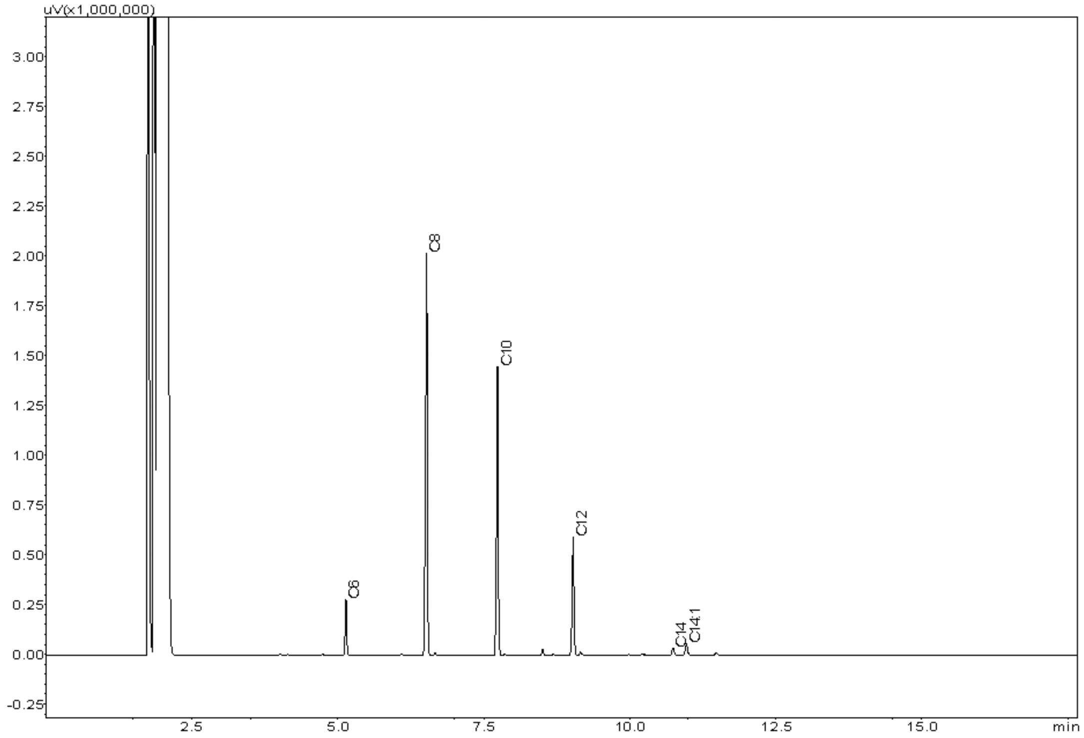
Retention Time (min)	Composition (wt %)	Compound ID	Monomer Name
5.14	5.85	C_6	3-hydroxyhexanoic acid
6.53	46.29	C_8	3-hydroxyoctanoic acid
7.74	30.96	C_{10}	3-hydroxydecanoic acid
9.03	13.82	C_{12}	3-hydroxydodecanoic acid
10.74	1.25	C_{14}	3-hydroxytetradecanoic acid
10.98	1.83	$C_{14:1}$	3-hydroxytetradecenoic acid

F.7 Gas chromatogram of 160 ℃-treated SPKO-derived PHA



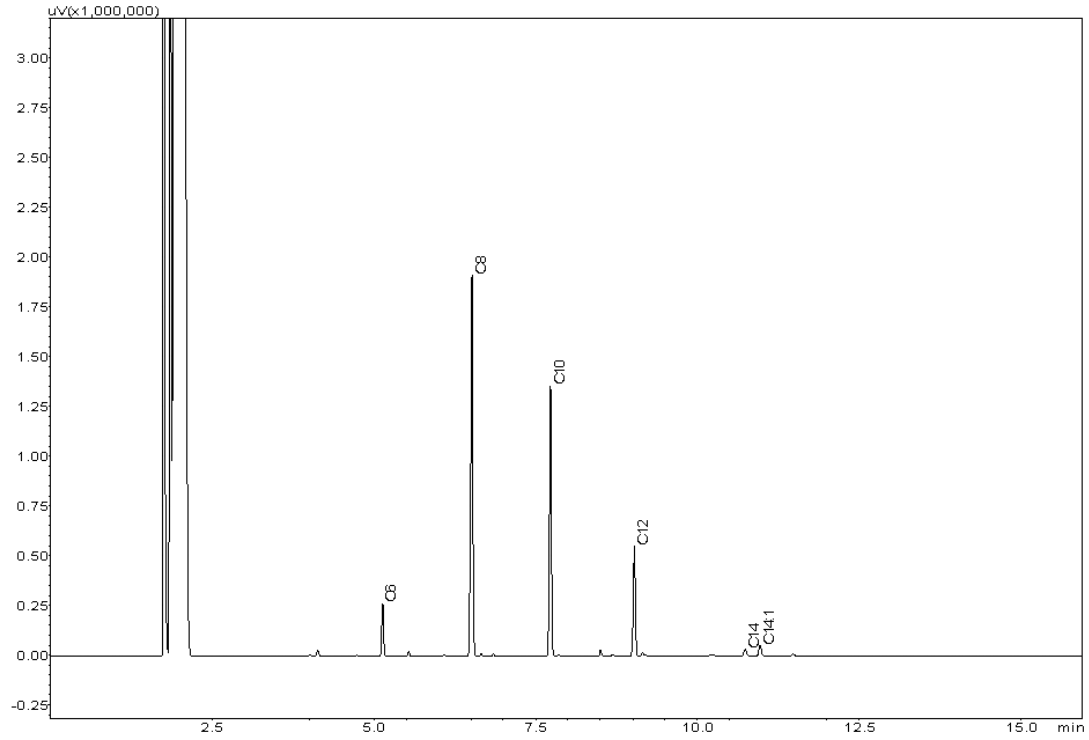
Retention Time (min)	Composition (wt %)	Compound ID	Monomer Name
5.14	5.73	C_6	3-hydroxyhexanoic acid
6.52	45.94	C_8	3-hydroxyoctanoic acid
7.74	31.10	C_{10}	3-hydroxydecanoic acid
9.03	14.18	C_{12}	3-hydroxydodecanoic acid
10.74	1.22	C_{14}	3-hydroxytetradecanoic acid
10.97	1.83	$C_{14:1}$	3-hydroxytetradecenoic acid

F.8 Gas chromatogram of 170 ℃-treated SPKO-derived PHA



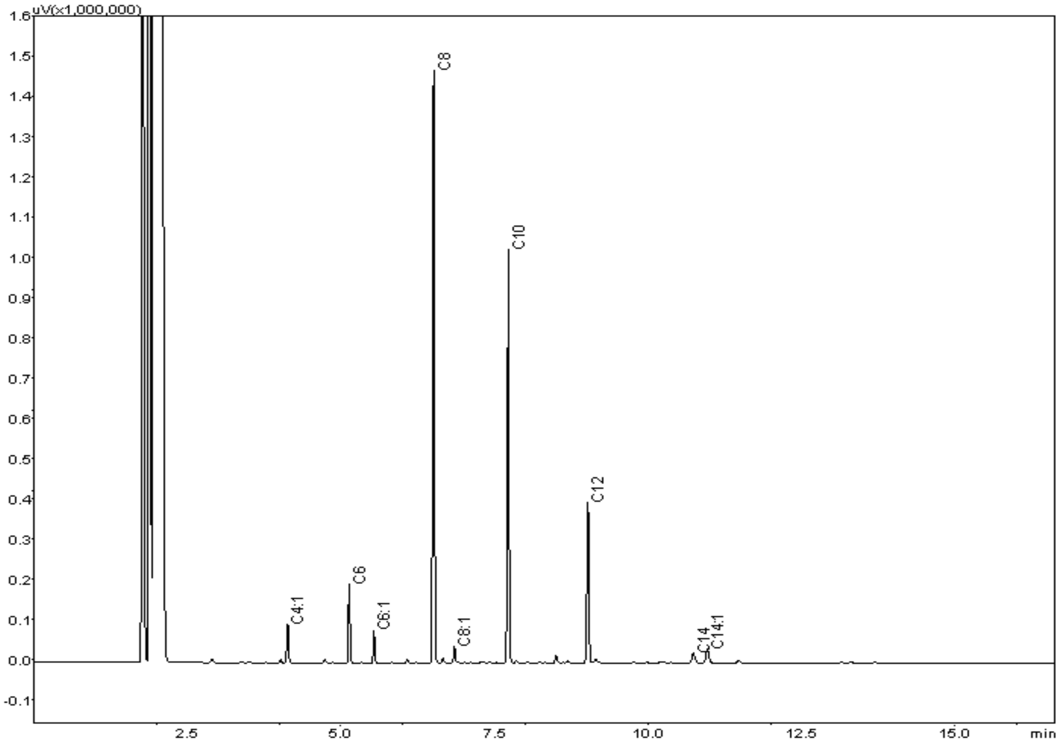
Retention Time (min)	Composition (wt %)	Compound ID	Monomer Name
5.14	5.76	C_6	3-hydroxyhexanoic acid
6.52	46.05	C_8	3-hydroxyoctanoic acid
7.74	31.06	C_{10}	3-hydroxydecanoic acid
9.03	13.97	C_{12}	3-hydroxydodecanoic acid
10.74	1.29	C_{14}	3-hydroxytetradecanoic acid
10.97	1.87	$C_{14:1}$	3-hydroxytetradecenoic acid

F.9 Gas chromatogram of 180 ℃-treated SPKO-derived PHA



Retention Time (min)	Composition (wt %)	Compound ID	Monomer Name
5.14	5.77	C_6	3-hydroxyhexanoic acid
6.52	46.15	C_8	3-hydroxyoctanoic acid
7.73	31.05	C_{10}	3-hydroxydecanoic acid
9.03	13.82	C_{12}	3-hydroxydodecanoic acid
10.74	1.35	C_{14}	3-hydroxytetradecanoic acid
10.97	1.86	$C_{14:1}$	3-hydroxytetradecenoic acid

F.10 Gas chromatogram of 190 ℃-treated SPKO-derived PHA

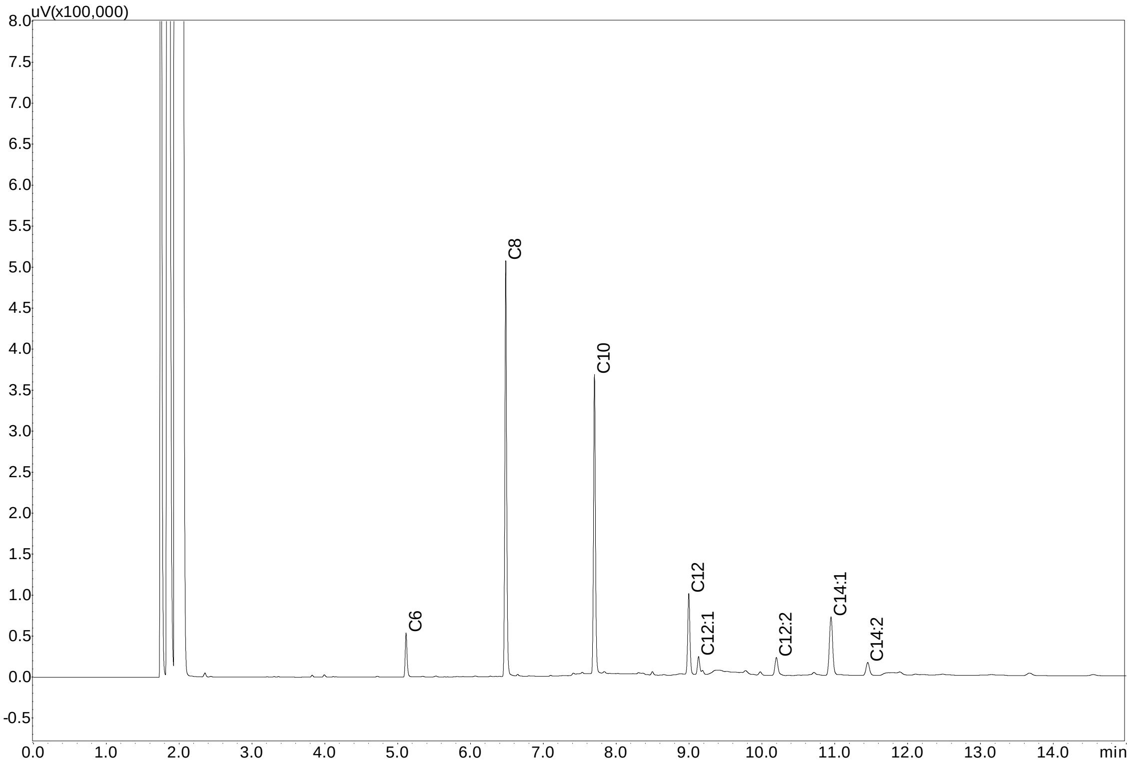


Retention Time (min)	Composition (wt %)	Compound ID	Monomer Name
4.14	2.95	$C_{4:1}$	3-hydroxybutenoic acid
5.14	5.45	C_6	3-hydroxyhexanoic acid
5.54	2.18	$C_{6:1}$	3-hydroxyhexenoic acid
6.51	43.18	C_8	3-hydroxyoctanoic acid
6.85	1.30	$C_{8:!}$	3-hydroxyoctenoic acid
7.73	28.97	C_{10}	3-hydroxydecanoic acid
9.02	12.80	C_{12}	3-hydroxydodecanoic acid
10.74	1.46	C_{14}	3-hydroxytetradecanoic acid
10.97	1.71	$C_{14:1}$	3-hydroxytetradecenoic acid

APPENDIX G:

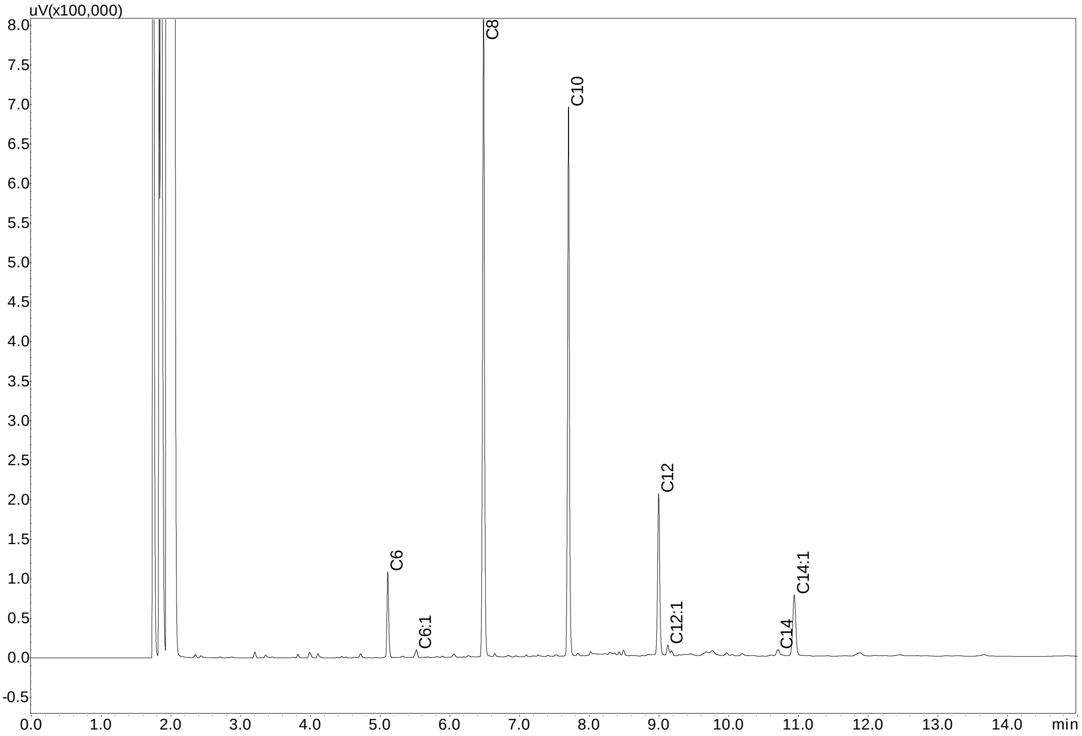
Gas chromatograms of mcl-PHA used in polymer blending

G.1 Gas chromatogram of OA-derived PHA



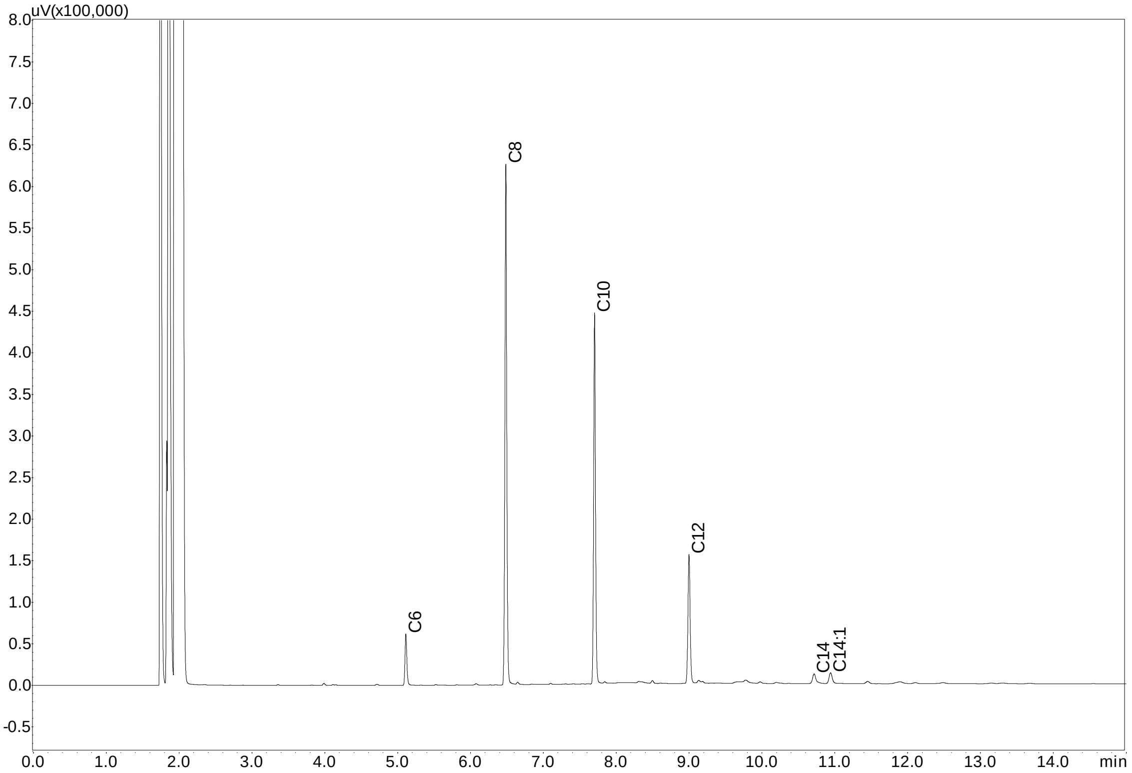
Retention Time (min)	**Composition (wt %)**	**Compound ID**	**Monomer name**
5.12	4.26	C_6	3-hydroxyhexanoic acid
6.48	39.42	C_8	3-hydroxyoctanoic acid
7.70	29.70	C_{10}	3-hydroxydecanoic acid
8.99	9.21	C_{12}	3-hydroxydodecanoic acid
9.13	2.16	$C_{12:1}$	3-hydroxydodecenoic acid
10.20	2.92	$C_{12:2}$	3-hydroxydodecadienoic acid
10.95	10.01	$C_{14:1}$	3-hydroxytetradecenoic acid
11.45	2.32	$C_{14:2}$	3-hydroxytetradecadienoic acid

G.2 Gas chromatogram of 170 ℃-treated OA-derived PHA



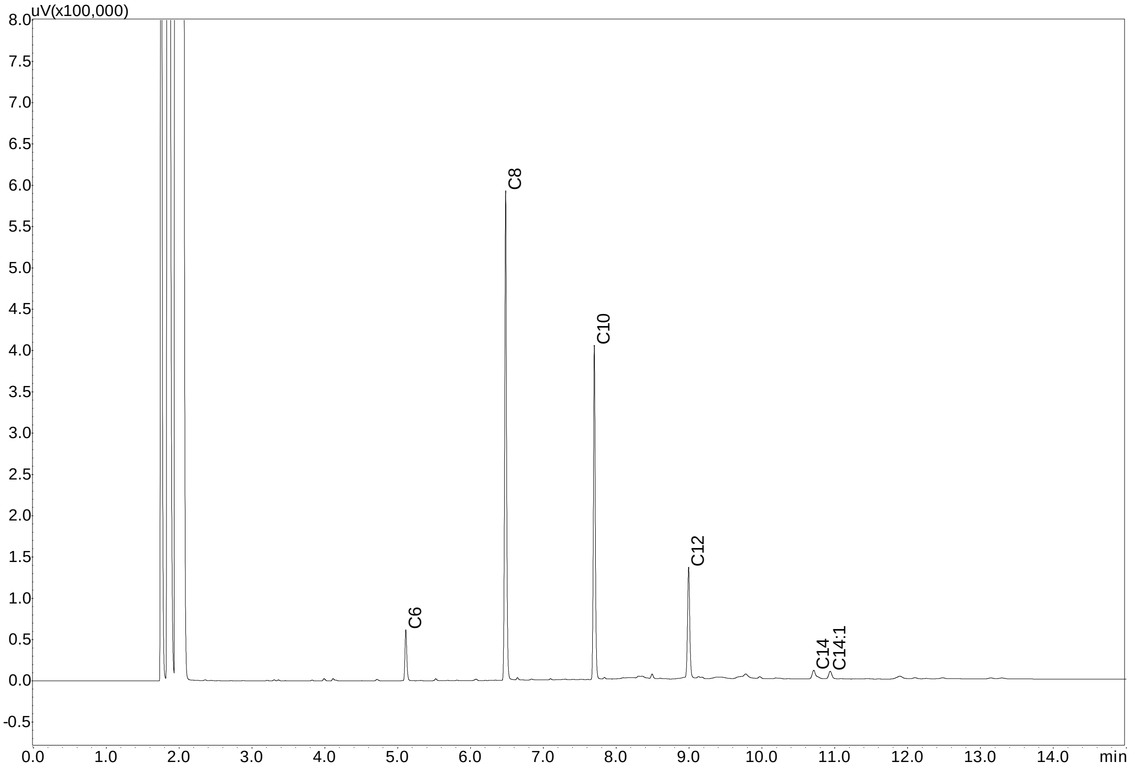
Retention Time (min)	Composition (wt %)	Compound ID	Monomer Name
5.11	5.03	C_6	3-hydroxyhexanoic acid
5.52	0.58	$C_{6:1}$	3-hydroxyhexenoic acid
6.48	41.81	C_8	3-hydroxyoctanoic acid
7.70	33.62	C_{10}	3-hydroxydecanoic acid
8.99	11.53	C_{12}	3-hydroxydodecanoic acid
9.13	0.75	$C_{12:1}$	3-hydroxydodecenoic acid
10.71	0.55	C_{14}	3-hydroxytetradecanoic acid
10.94	6.13	$C_{14:1}$	3-hydroxytetradecenoic acid

G.3 Gas chromatogram of SPKO-derived PH**A**



Retention Time (min)	Composition (wt %)	Compound ID	Monomer Name
5.11	4.51	C_6	3-hydroxyhexanoic acid
6.49	46.29	C_8	3-hydroxyoctanoic acid
7.70	32.59	C_{10}	3-hydroxydecanoic acid
8.99	13.42	C_{12}	3-hydroxydodecanoic acid
10.72	1.60	C_{14}	3-hydroxytetradecanoic acid
10.94	1.59	$C_{14:1}$	3-hydroxytetradecenoic acid

G.4 Gas chromatogram of 170 ℃-treated SPKO-derived PHA

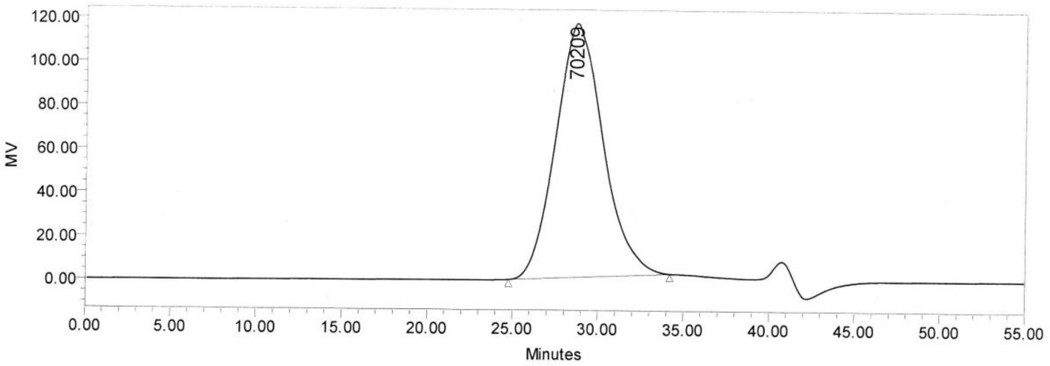


Retention Time (min)	**Composition (wt %)**	**Compound ID**	**Monomer Name**
5.11	4.86	C_6	3-hydroxyhexanoic acid
6.48	47.21	C_8	3-hydroxyoctanoic acid
7.70	32.36	C_{10}	3-hydroxydecanoic acid
8.99	12.59	C_{12}	3-hydroxydodecanoic acid
10.71	1.74	C_{14}	3-hydroxytetradecanoic acid
10.94	1.24	$C_{14:1}$	3-hydroxytetradecenoic acid

APPENDIX H:

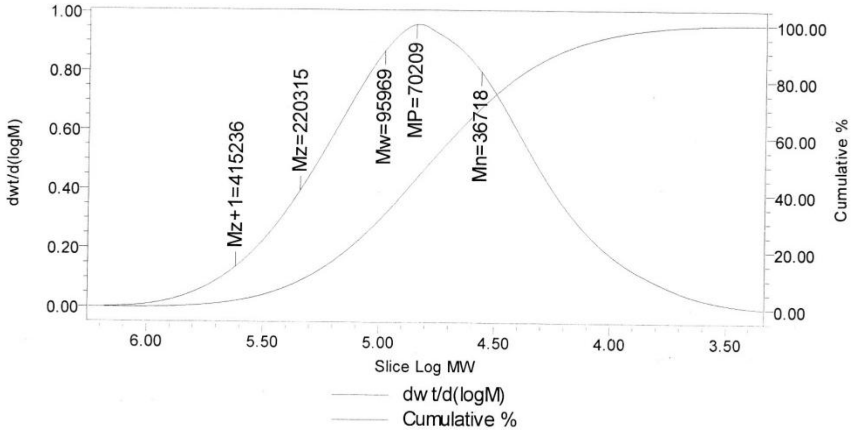
Gas permeation chromatograms of PVC and mcl-PHA used in polymer blending

H.1 Gas permeation chromatogram of PVC

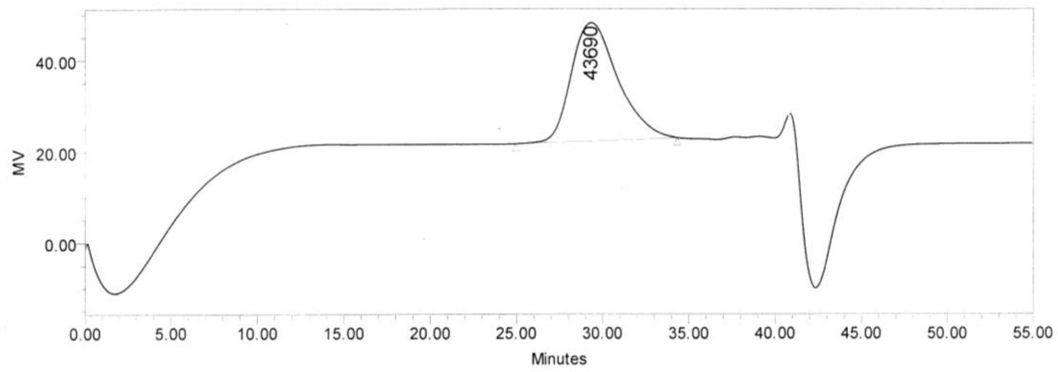


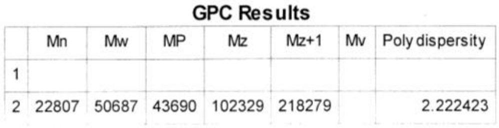
GPC Results

	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity
1	36718	95969	70209	220315	415236		2.613656
2							



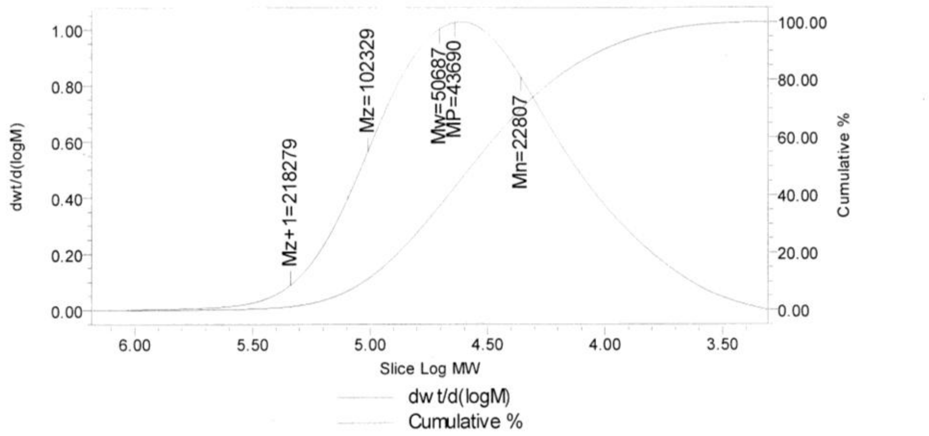
H.2 Gas permeation chromatogram of OA-derived PHA



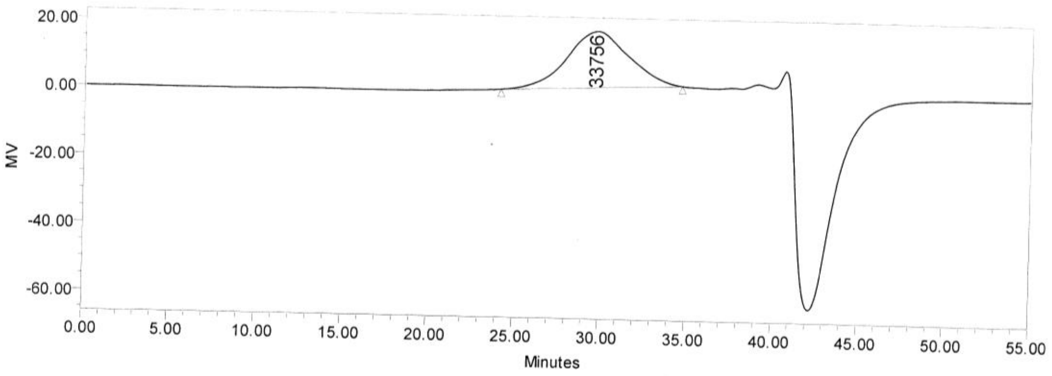


GPC Results

	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity
1							
2	22807	50687	43690	102329	218279		2.222423

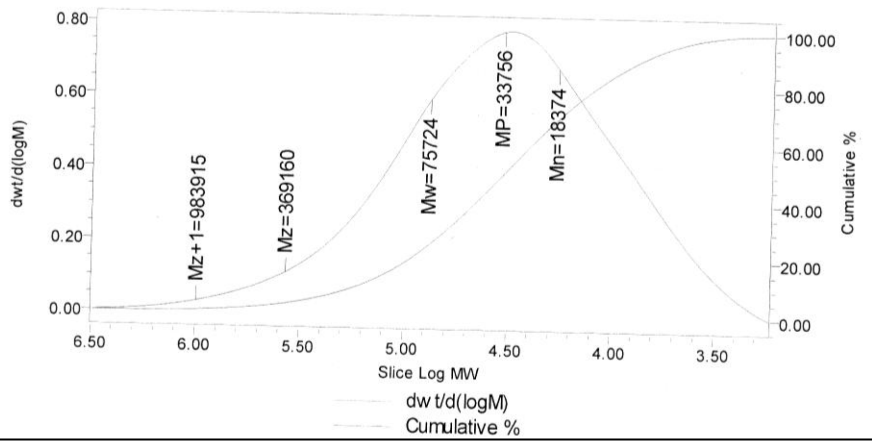


H.3 Gas permeation chromatogram of 170 ℃-treated OA-derived PHA

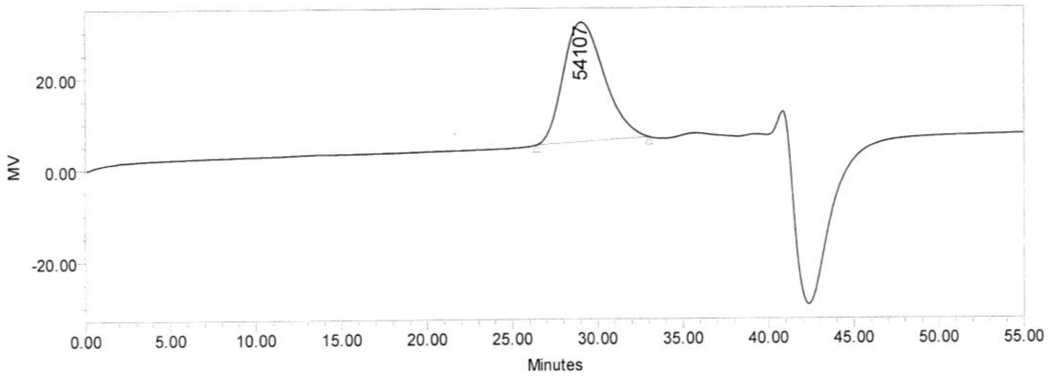


GPC Results

	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity
1	18374	75724	33756	369160	983915		4.121263
2							

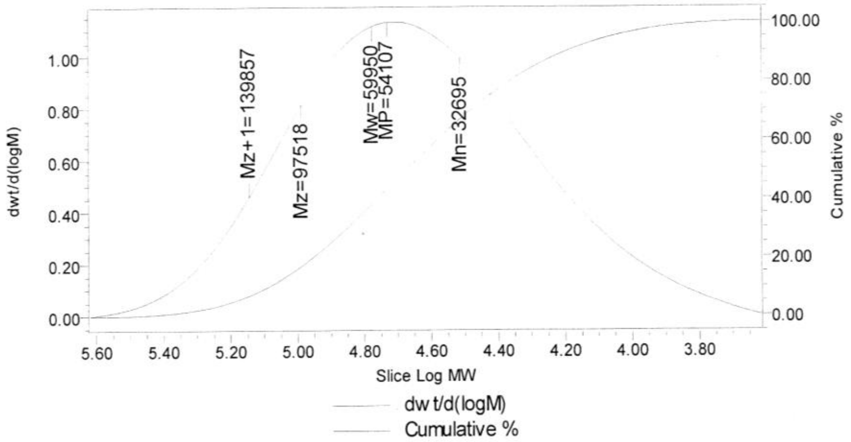


H.4 Gas permeation chromatogram of SPKO-derived PHA

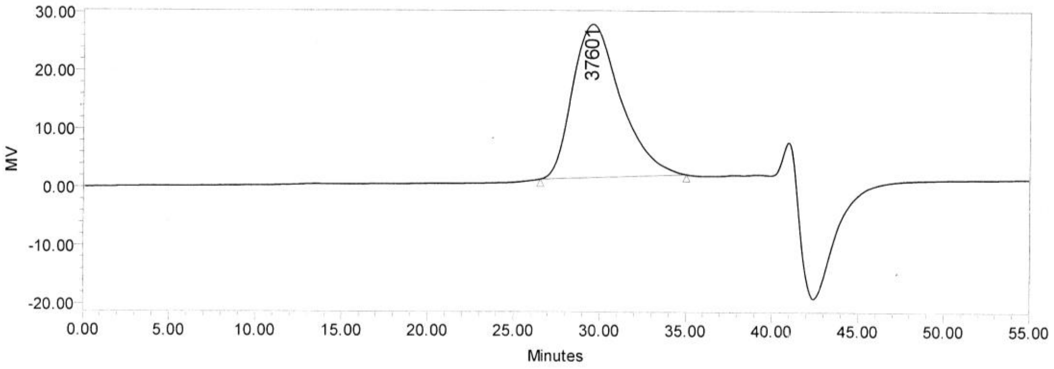


GPC Results

	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity
1	32695	59950	54107	97518	139857		1.833600
2							

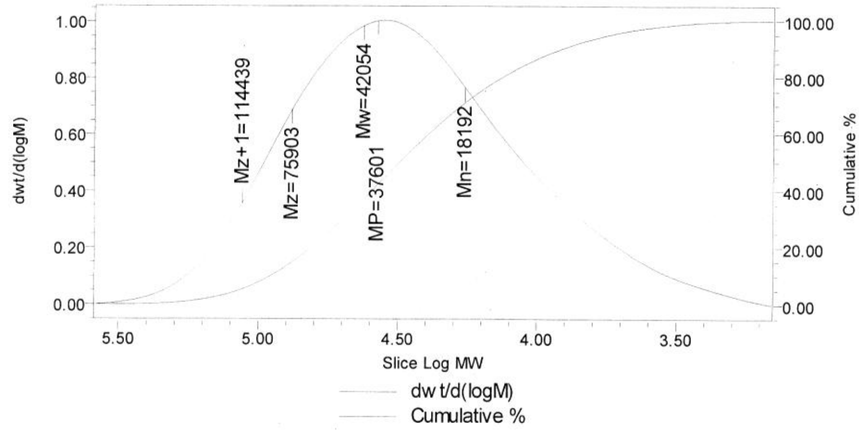


H.5 Gas permeation chromatogram of 170 ℃-treated SPKO-derived PHA



GPC Results

	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity
1	18192	42054	37601	75903	114439		2.311645
2							

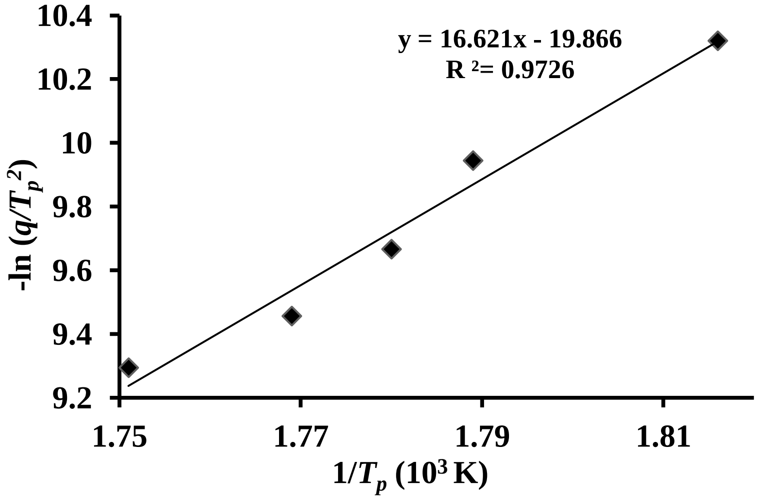


APPENDIX I:

Determination of kinetic parameters for PVC and PVC/PHA polymer blends during thermal degradation

I.1 Descriptions of calculations of E_d, A and ΔS for PVC during first stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	550.73	1.816	303303.5329	3.297	10.320
15	558.95	1.789	312425.1025	4.801	9.944
20	561.69	1.780	315495.6561	6.339	9.666
25	565.42	1.769	319699.7764	7.820	9.456
30	571.02	1.751	326063.8404	9.201	9.294



Equation for the Kissinger plot: Y = 16.621X-19.866 ($R^2 = 0.9726$)

With gradient, $E_d/R = 16.621 \times 10^3$ K

$E_d = 16621$ K x 8.3143 J K^{-1} mol^{-1}
= 138191.9803 J mol^{-1}
= 138.2 kJ mol^{-1}

With intersection of y-axis, $\ln(AR/E_d) = 19.866$

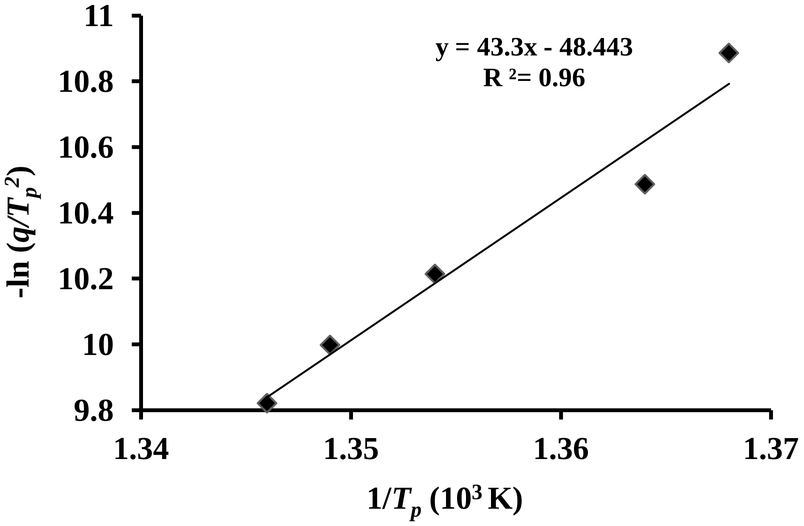
$AR/E_d = e^{19.866}$
$A = E_d/R \times e^{19.866}$
$= 16621 \times e^{19.866}$ min^{-1}
$= 7.05 \times 10^{12}$ min^{-1}
$= 7.05 \times 10^{12}/60$ s
$= 1.18 \times 10^{11}$ s^{-1}

At 10 ℃ min^{-1}, T_p=550.73 K,

ΔS= 8.3143 J K^{-1} mol^{-1} x ln(1.18x10^{11} s^{-1})(6.626x10^{-34} Js)/(1.3807x10^{-23} J K^{-1})(550.73 K)
= 8.3143 J K^{-1} mol^{-1} x ln(5.663 x 1.816x10^{-3}
= -38.1 J K^{-1} mol^{-1}

I.2 Descriptions of calculations of E_d, A and ΔS for PVC during second stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	730.08	1.369	533016.8064	1.876	10.884
15	733.15	1.364	537508.9225	2.791	10.487
20	738.74	1.354	545736.7876	3.665	10.214
25	741.21	1.349	549392.2641	4.550	9.998
30	743.15	1.346	552271.9225	5.432	9.821



Equation for the Kissinger plot: Y = 43.3X-48.443   ($R^2 = 0.96$)

With gradient, $E_d/R = 43.3 \times 10^3$ K

$$E_d = 43300 \text{ K} \times 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$= 360009.19 \text{ J mol}^{-1}$$
$$= 360 \text{ kJ mol}^{-1}$$

With intersection of y-axis, $\ln(AR/E_d) = 48.443$

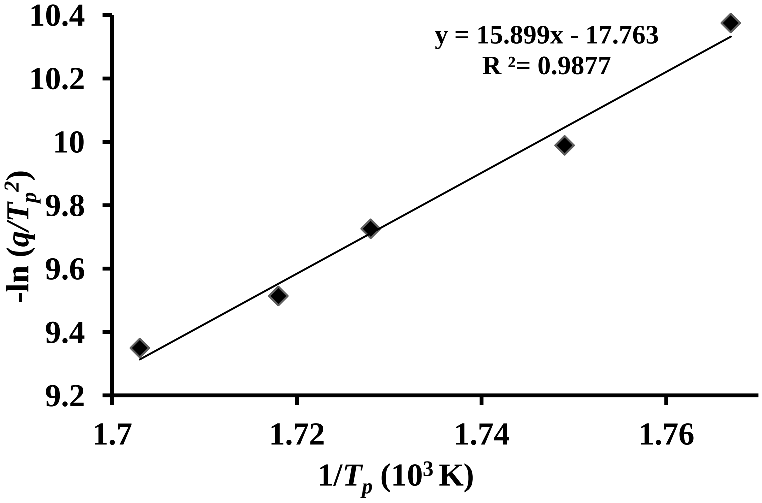
$$AR/E_d = e^{48.443}$$
$$A = E_d/R \times e^{48.443}$$
$$= 43300 \times e^{48.443} \text{ min}^{-1}$$
$$= 4.73 \times 10^{25} \text{ min}^{-1}$$
$$= 4.73 \times 10^{25}/60 \text{ s}$$
$$= 7.89 \times 10^{23} \text{ s}^{-1}$$

At 10 °C min^{-1}, T_p=731.98 K,

$$\Delta S = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln(7.89\text{x}10^{23} \text{ s}^{-1})(6.626\text{x}10^{-34} \text{ Js})/(1.3807\text{x}10^{-23} \text{ J K}^{-1})(731.08 \text{ K})$$
$$= 8.3143 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln(3.786\text{x}10^{13} \times 1.368\text{x}10^{-3})$$
$$= 205.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

I.3 Descriptions of calculations of E_d, A and ΔS for PVC/$PHA_{OA\text{-}2.5}$ during first stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	566.05	1.767	320412.6025	3.121	10.375
15	571.67	1.749	326806.5889	4.590	9.989
20	578.65	1.728	334835.8225	5.973	9.726
25	582.09	1.718	338828.7681	7.378	9.514
30	587.22	1.703	344827.3284	8.700	9.350



Equation for the Kissinger plot: Y = 15.899X – 17.763 (R^2 = 0.9877)

With gradient, E_d/R =15.899 x 10^3 K
E_d= 15899 K x 8.3143 J K^{-1} mol^{-1}
= 132189.0557 J mol^{-1}
= 132.2 kJ mol^{-1}

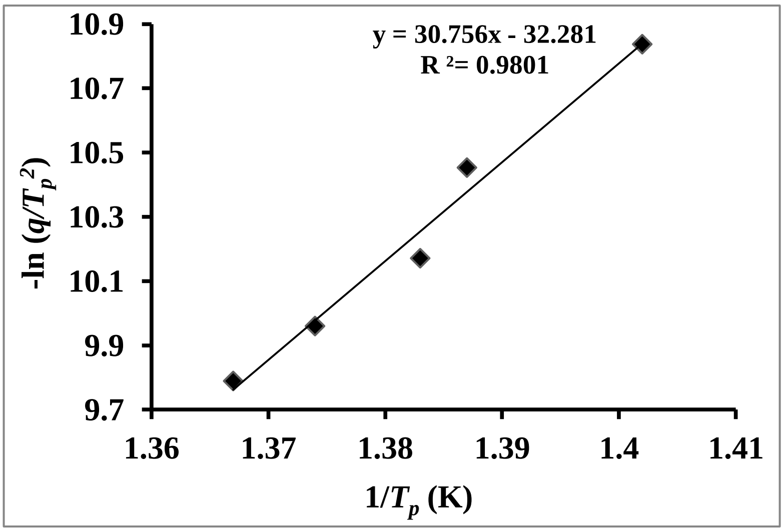
With intersection of y-axis, $\ln(AR/E_d)$ = 17.763
$AR/E_d = e^{17.763}$
$A = E_d/R \times e^{17.763}$
= 14020 x $e^{17.763}$ min^{-1}
= 8.24 x 10^{11} min^{-1}
= 8.24 x 10^{11} /60 s
= 1.37 x 10^{10} s^{-1}

At 10 °C min^{-1}, T_p=566.05 K,

ΔS= 8.3143 J K^{-1} mol^{-1} x ln(1.37x10^{10} s^{-1})(6.626x10^{-34} Js)/(1.3807x10^{-23} J K^{-1})(566.05 K)
= 8.3143 J K^{-1} mol^{-1} x ln(6.575x10^{-1} x 1.767x10^{-3})
= -56.2 J K^{-1} mol^{-1}

I.4 Descriptions of calculations of E_d, A and ΔS for PVC/PHA$_{OA-2.5}$ during second stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	713.16	1.402	508597.1856	1.966	10.837
15	720.77	1.387	519509.3929	2.887	10.453
20	723.01	1.383	522743.4601	3.826	10.171
25	727.55	1.374	529329.0025	4.723	9.960
30	731.36	1.367	534887.4496	5.609	9.789



Equation for the Kissinger plot: Y = 30.756X – 32.281 ($R^2 = 0.9801$)

With gradient, E_d/R =30.756 x 10^3 K

E_d= 30756 K x 8.3143 J K^{-1} mol^{-1}

= 255714.6108 J mol^{-1}

= 255.7 kJ mol^{-1}

With intersection of y-axis, $\ln(AR/E_d) = 32.281$

$AR/E_d = e^{32.281}$

$A = E_d/R \times e^{32.281}$

$= 30756 \times e^{32.281}$ min^{-1}

$= 3.22 \times 10^{18}$ min^{-1}

$= 3.22 \times 10^{18}$ /60 s

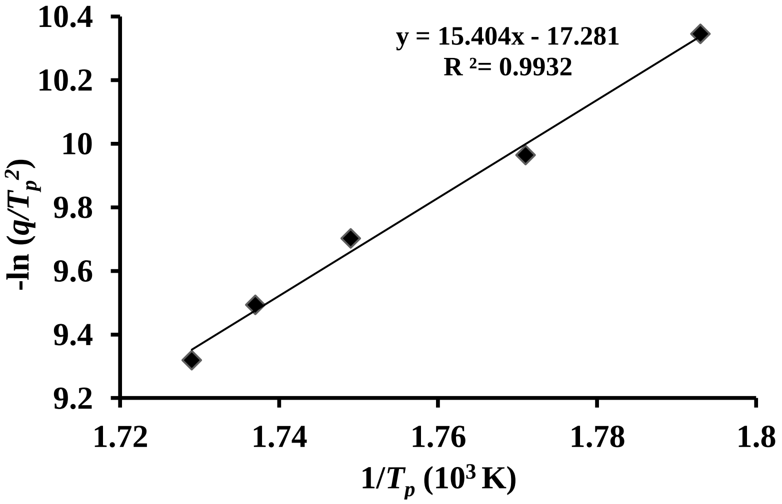
$= 5.36 \times 10^{16}$ s^{-1}

At 10 °C min^{-1}, T_p=713.16 K,

ΔS= 8.3143 J K^{-1} mol^{-1} x ln(5.36x10^{16} s^{-1})(6.626x10^{-34} Js)/(1.3807x10^{-23} J K^{-1})(713.16 K)
= 8.3143 J K^{-1} mol^{-1} x ln(2.572x10^{6} x 1.402x10^{-3})
= 68.1 J K^{-1} mol^{-1}

I.5 Descriptions of calculations of E_d, A and ΔS for PVC/PHA$_{OA-5}$ during first stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	557.66	1.793	310984.6756	3.216	10.345
15	564.54	1.771	318705.4116	4.707	9.964
20	571.74	1.749	326886.6276	6.118	9.702
25	575.84	1.737	331591.7056	7.539	9.493
30	578.33	1.729	334465.5889	8.970	9.319



Equation for the Kissinger plot: Y = 15.404X – 17.281 (R^2 = 0.9932)

With gradient, E_d/R = 15.404 x 10^3 K

E_d= 15404 K x 8.3143 J K^{-1} mol^{-1}
= 128073.4772 J mol^{-1}
= 128.1 kJ mol^{-1}

With intersection of y-axis, $\ln(AR/E_d)$ = 17.281

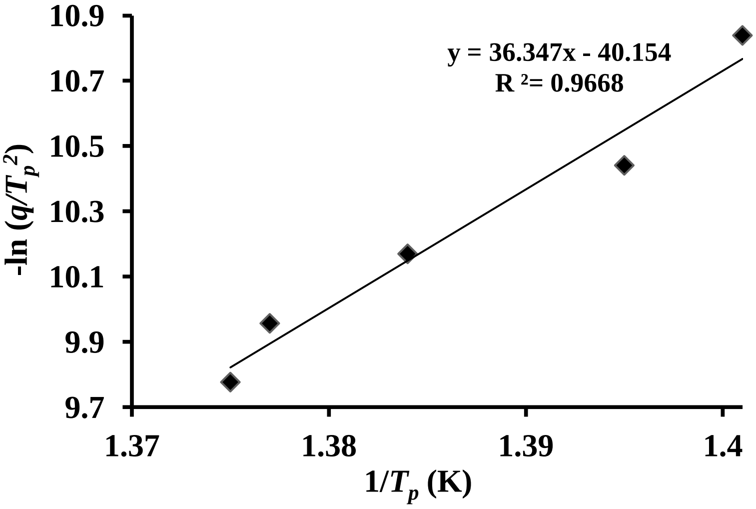
$AR/E_d = e^{17.281}$
$A = E_d/R$ x $e^{17.281}$
= 15404 x $e^{17.281}$ min^{-1}
=4.93 x 10^{11} min^{-1}
=4.93 x 10^{11}/60 s
= 8.21 x 10^9 s^{-1}

At 10 ℃ min^{-1}, T_p=557.66 K,

ΔS= 8.3143 J K^{-1} mol^{-1} x ln(8.21x10^9 s^{-1})(6.626x10^{-34} Js)/(1.3807x10^{-23} J K^{-1})(557.66 K)
= 8.3143 J K^{-1} mol^{-1} x ln(0.394 x 1.793x10^{-3})
= -60.3 J K^{-1} mol^{-1}

I.6 Descriptions of calculations of E_d, A and ΔS for PVC/PHA$_{OA-5}$ during second stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	713.85	1.401	509581.8225	1.962	10.839
15	716.66	1.395	513601.5556	2.291	10.441
20	722.45	1.384	521934.0025	3.832	10.170
25	726.40	1.377	527656.9600	4.738	9.957
30	727.29	1.375	528950.7441	5.672	9.777



Equation for the Kissinger plot: Y = 36.347X – 40.154 ($R^2 = 0.9668$)

With gradient, $E_d/R = 36.347 \times 10^3$ K

$E_d = 36347 \text{ K} \times 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$

$= 302199.8621 \text{ J mol}^{-1}$

$= 302.2 \text{ kJ mol}^{-1}$

With intersection of y-axis, $\ln(AR/E_d) = 40.154$

$AR/E_d = e^{40.154}$

$A = E_d/R \times e^{40.154}$

$= 36347 \times e^{40.154} \text{ min}^{-1}$

$= 9.98 \times 10^{21} \text{ min}^{-1}$

$= 9.98 \times 10^{21}/60 \text{ s}$

$= 1.66 \times 10^{20} \text{ s}^{-1}$

At 10 ℃ min^{-1}, T_p=713.85 K,

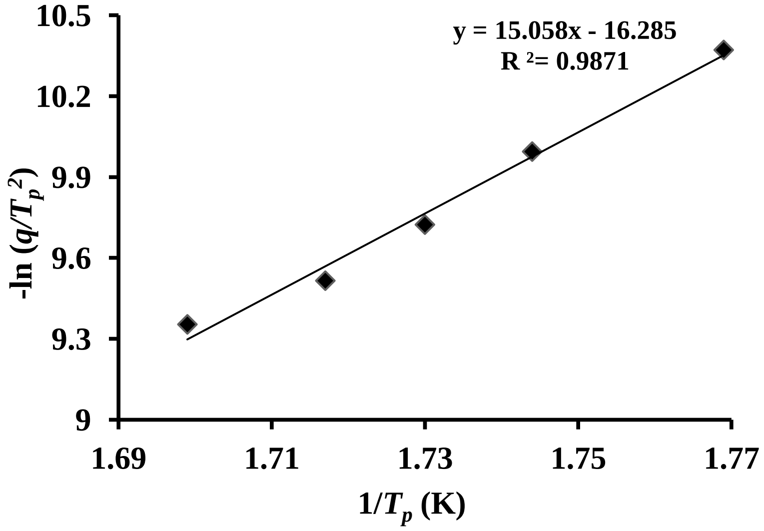
$\Delta S = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln(1.66\text{x}10^{20} \text{ s}^{-1})(6.626\text{x}10^{-34} \text{ Js})/(1.3807\text{x}10^{-23} \text{ J K}^{-1})(713.85 \text{ K})$

$= 8.3143 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln(7.966\text{x}10^{9} \times 1.401\text{x}10^{-3})$

$= 134.9 \text{ J K}^{-1} \text{ mol}^{-1}$

I.7 Descriptions of calculations of E_d, A and ΔS for PVC/degPHA$_{OA\text{-}2.5}$ during first stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	565.32	1.769	319586.7024	3.129	10.372
15	573.24	1.744	328604.0976	4.565	9.995
20	576.92	1.733	332836.6864	6.009	9.720
25	584.45	1.711	341581.8025	7.319	9.522
30	588.55	1.699	346391.1025	8.661	9.354



Equation for the Kissinger plot: Y = 15.058X – 16.285 (R^2 = 0.9871)

With gradient, E_d/R = 15.058 x 10^3 K

E_d= 15058 K x 8.3143 J K^{-1} mol^{-1}

= 125196.7294 J mol^{-1}

= 125.2 kJ mol^{-1}

With intersection of y-axis, $\ln(AR/E_d)$ = 16.285

AR/E_d = $e^{16.285}$

$A = E_d/R$ x $e^{16.285}$

= 15058 x $e^{16.285}$ min^{-1}

= 1.78 x 10^{11} min^{-1}

= 1.78 x 10^{11}/60 s

= 2.97 x 10^9 s^{-1}

At 10 ℃ min^{-1}, T_p=565.32 K,

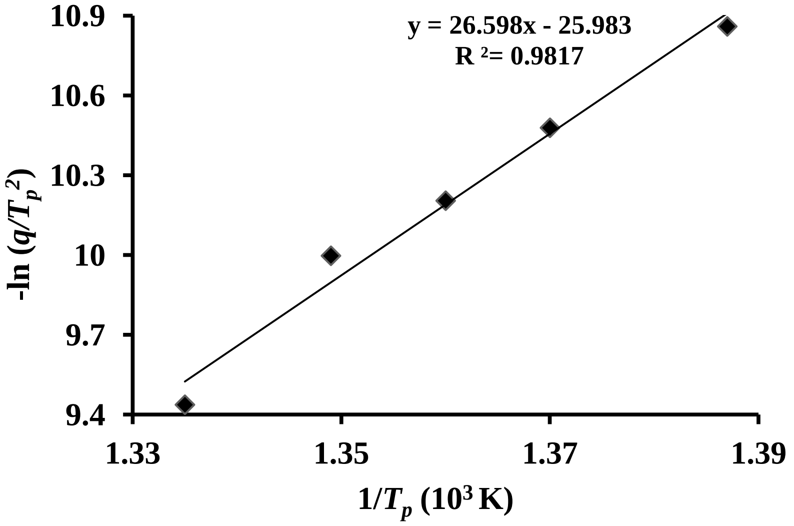
ΔS= 8.3143 J K^{-1} mol^{-1} x ln(2.97x10^9 s^{-1})(6.626x10^{-34} Js)/(1.3807x10^{-23} J K^{-1})(565.32 K)

= 8.3143 J K^{-1} mol^{-1} x ln(0.1425 x 1.769x10^{-3})

= -68.9 J K^{-1} mol^{-1}

I.8 Descriptions of calculations of E_d, A and ΔS for PVC/degPHA$_{OA\text{-}2.5}$ during second stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	721.06	1.387	519927.5236	1.923	10.859
15	729.80	1.370	532608.0400	2.816	10.478
20	735.11	1.360	540386.7121	3.701	10.204
25	741.12	1.349	549258.8544	4.552	9.997
30	749.31	1.335	561465.4761	5.343	9.437



Equation for the Kissinger plot: Y = 26.598X – 25.983 (R^2 = 0.9817)

With gradient, $E_d/R = 26.598 \times 10^3$ K

E_d= 26.598 K x 8.3143 J K^{-1} mol^{-1}

= 221143.7514 J mol^{-1}

= 221.1 kJ mol^{-1}

With intersection of y-axis, $\ln(AR/E_d) = 25.983$

$AR/E_d = e^{25.983}$

$A = E_d/R \times e^{25.983}$

$= 26598 \times e^{25.983}$ min^{-1}

$= 5.12 \times 10^{15}$ min^{-1}

$= 5.12 \times 10^{15}/60$ s

$= 8.53 \times 10^{13}$ s^{-1}

At 10 °C min^{-1}, T_p=721.06 K,

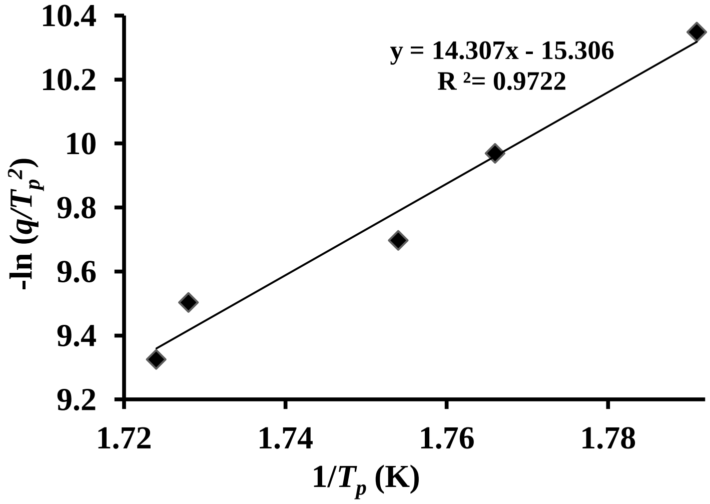
ΔS= 8.3143 J K^{-1} mol^{-1} x ln(8.53x10^{13} s^{-1})(6.626x10^{-34} Js)/(1.3807x10^{-23} J K^{-1})(721.06 K)

= 8.3143 J K^{-1} mol^{-1} x ln(4093.56 x 1.3807x10^{-3})

= 14.4 J K^{-1} mol^{-1}

I.9 Descriptions of calculations of E_d, A and ΔS for PVC/degPHA$_{OA\text{-}5}$ during first stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	558.49	1.791	311911.0801	3.206	10.348
15	566.10	1.766	320469.2100	4.681	9.969
20	570.08	1.754	324991.2064	6.154	9.696
25	578.86	1.728	335078.8996	7.461	9.503
30	579.95	1.724	336342.0025	8.919	9.325



Equation for the Kissinger plot: Y = 14.307X – 15.306 (R^2 = 0.9722)

With gradient, $E_d/R = 14.307 \times 10^3$ K

$E_d = 14307\text{ K} \times 8.3143\text{ J K}^{-1}\text{ mol}^{-1}$

$= 118952.6901\text{ J mol}^{-1}$

$= 119.0\text{ kJ mol}^{-1}$

With intersection of y-axis, $\ln(AR/E_d) = 15.306$

$AR/E_d = e^{15.306}$

$A = E_d/R \times e^{15.306}$

$= 14307 \times e^{15.306}\text{ min}^{-1}$

$= 6.35 \times 10^{10}\text{ min}^{-1}$

$= 6.35 \times 10^{10}/60\text{ s}$

$= 1.06 \times 10^9\text{ s}^{-1}$

At 10 ℃ min^{-1}, T_p=558.49 K,

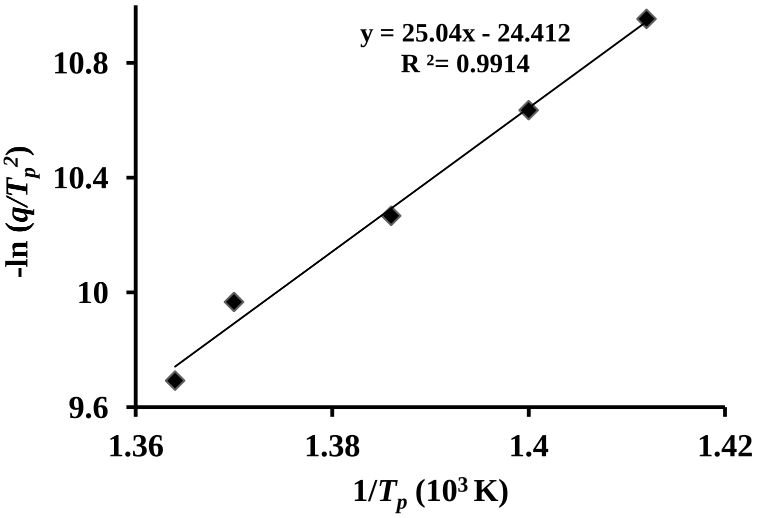
$\Delta S = 8.3143\text{ J K}^{-1}\text{ mol}^{-1} \times \ln(1.06\times10^9\text{ s}^{-1})(6.626\times10^{-34}\text{ Js})/(1.3807\times10^{-23}\text{ J K}^{-1})(558.49\text{ K})$

$= 8.3143\text{ J K}^{-1}\text{ mol}^{-1} \times \ln(0.0509 \times 1.791\times10^{-3})$

$= -77.3\text{ J K}^{-1}\text{ mol}^{-1}$

I.10 Descriptions of calculations of E_d, A and ΔS for PVC/degPHA$_{OA\text{-}5}$ during second stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	708.27	1.412	501646.3929	1.993	10.953
15	714.37	1.400	510324.4969	2.939	10.635
20	721.51	1.386	520576.6801	3.842	10.267
25	729.95	1.370	532827.0025	4.692	9.967
30	733.12	1.364	537464.9344	5.582	9.693



Equation for the Kissinger plot: Y = 25.04X – 24.412 (R^2 = 0.9914)

With gradient, E_d/R = 25.04 x 10^3 K

E_d= 25040 K x 8.3143 J K^{-1} mol^{-1}

= 208190.072 J mol^{-1}

= 208.2 kJ mol^{-1}

With intersection of y-axis, $\ln(AR/E_d)$ = 24.412

AR/E_d = $e^{24.412}$

A = E_d/R x $e^{24.412}$

= 25040 x $e^{24.412}$ min^{-1}

= 1 x 10^{15} min^{-1}

= 1 x 10^{15} /60 s

= 1.67 x 10^{13} s^{-1}

At 10 ℃ min^{-1}, T_p=708.27 K,

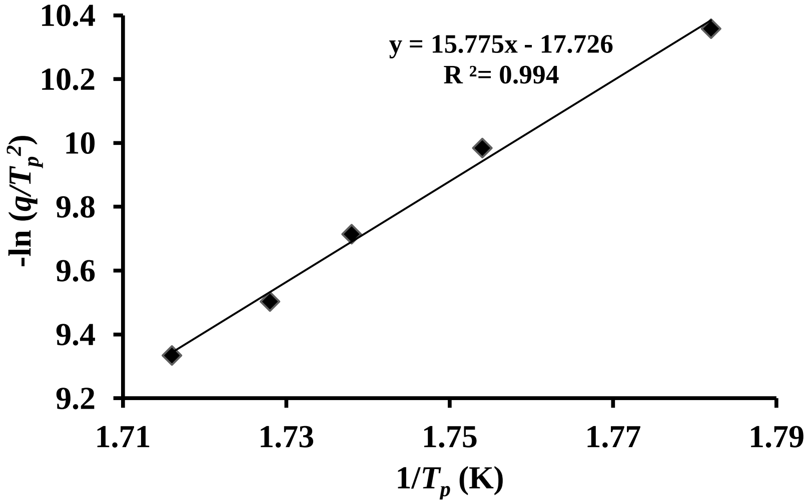
ΔS= 8.3143 J K^{-1} mol^{-1} x ln(1.67x10^{13} s^{-1})(6.626x10^{-34} Js)/(1.3807x10^{-23} J K^{-1})(708.27 K)

= 8.3143 J K^{-1} mol^{-1} x ln(801.4 x 1.412x10^{-3})

= 1.03 J K^{-1} mol^{-1}

I.11 Descriptions of calculations of E_d, A and ΔS for PVC/PHA$_{SPKO-2.5}$ during first stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	561.18	1.782	314922.9924	3.175	10.358
15	570.13	1.754	325048.2169	4.615	9.984
20	575.26	1.738	330924.0676	6.044	9.714
25	578.87	1.728	335090.4769	7.461	9.503
30	582.59	1.716	339411.1081	8.839	9.334



Equation for the Kissinger plot: Y = 15.775X – 17.726 (R^2 = 0.994)

With gradient, $E_d/R = 15.775 \times 10^3$ K

$E_d = 15775 \text{ K} \times 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$

$= 131158.0825 \text{ J mol}^{-1}$

$= 131.2 \text{ kJ mol}^{-1}$

With intersection of y-axis, $\ln(AR/E_d) = 17.726$

$AR/E_d = e^{17.726}$

$A = E_d/R \times e^{17.726}$

$= 15775 \times e^{17.726} \text{ min}^{-1}$

$= 7.88 \times 10^{11} \text{ min}^{-1}$

$= 7.88 \times 10^{11}/60$ s

$= 1.31 \times 10^{10} \text{ s}^{-1}$

At 10 ℃ min^{-1}, T_p=561.18 K,

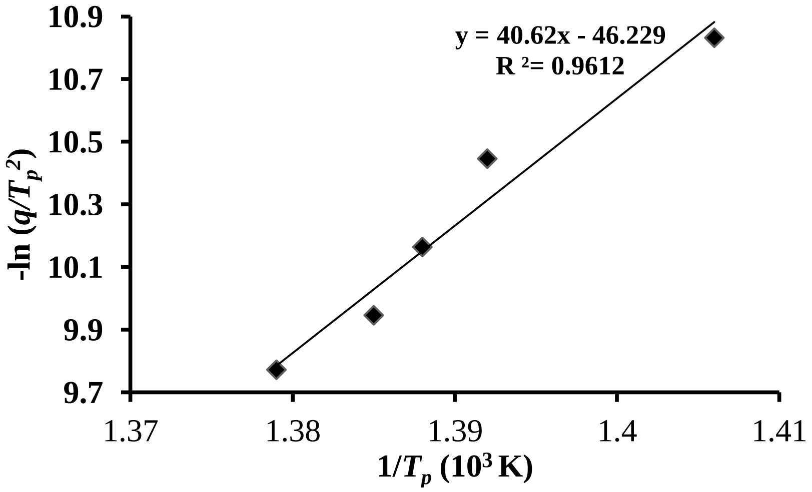
$\Delta S = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln(1.31\times10^{10} \text{ s}^{-1})(6.626\times10^{-34} \text{ Js})/(1.3807\times10^{-23} \text{ J K}^{-1})(561.18 \text{ K})$

$= 8.3143 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln(6.287\times10^{-1} \times 1.782\times10^{-3})$

$= -56.5 \text{ J K}^{-1} \text{ mol}^{-1}$

I.12 Descriptions of calculations of E_d, A and ΔS for PVC/PHA$_{SPKO-2.5}$ during second stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	711.32	1.406	505976.1424	1.976	10.832
15	718.38	1.392	516069.8244	2.907	10.446
20	720.44	1.388	519033.7936	3.853	10.164
25	722.16	1.385	521515.0656	4.794	9.946
30	725.36	1.379	526147.1296	5.702	9.772



Equation for the Kissinger plot: Y = 40620X – 46.229 (R^2 = 0.9612)

With gradient, $E_d/R = 40620 \times 10^3$ K
$E_d = 40620$ K x 8.3143 J K^{-1} mol^{-1}
= 337726.866 J mol^{-1}
= 337.7 kJ mol^{-1}

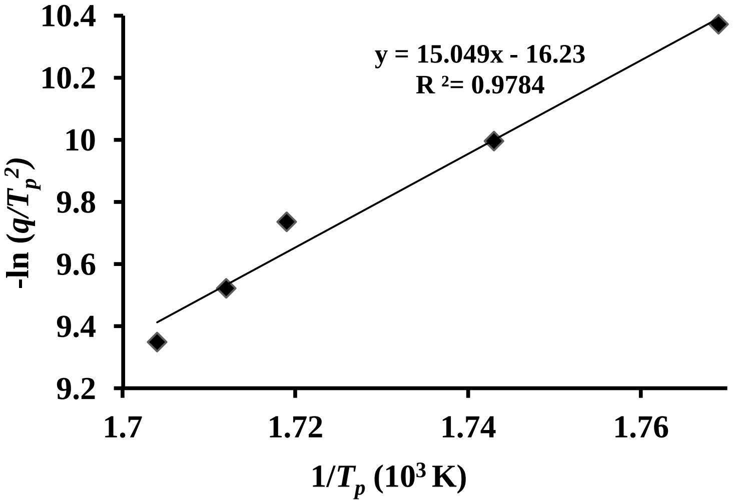
With intersection of y-axis, $\ln(AR/E_d) = 46.229$
$AR/E_d = e^{46.229}$
$A = E_d/R \times e^{46.229}$
$= 40620 \times e^{46.229}$ min^{-1}
$= 4.85 \times 10^{24}$ min^{-1}
$= 4.85 \times 10^{24}/60$ s
$= 8.08 \times 10^{22}$ s^{-1}

At 10 ℃ min^{-1}, T_p=711.32 K,

ΔS= 8.3143 J K^{-1} mol^{-1} x ln(8.08x10^{22} s^{-1})(6.626x10^{-34} Js)/(1.3807x10^{-23} J K^{-1})(711.32 K)
= 8.3143 J K^{-1} mol^{-1} x ln(3.878x10^{12} x 1.406x10^{-3})
= 186.4 J K^{-1} mol^{-1}

I.13 Descriptions of calculations of E_d, A and ΔS for PVC/PHA$_{SPKO-5}$ during first stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	565.29	1.769	319552.7841	3.129	10.372
15	573.76	1.743	329200.5376	4.556	9.996
20	581.63	1.719	338293.4569	5.912	9.736
25	584.27	1.712	341371.4329	7.323	9.522
30	586.98	1.704	344545.5204	8.707	9.349



Equation for the Kissinger plot: Y = 15.049X – 16.23 ($R^2 = 0.9784$)

With gradient, $E_d/R = 15.049 \times 10^3$ K

E_d= 15049 K x 8.3143 J K^{-1} mol^{-1}

= 125121.9007 J mol^{-1}

= 125.1 kJ mol^{-1}

With intersection of y-axis, $\ln(AR/E_d) = 16.23$

$AR/E_d = e^{16.23}$

$A = E_d/R \times e^{16.23}$

$= 15049 \times e^{16.23}$ min^{-1}

$=1.68 \times 10^{11}$ min^{-1}

$=1.68 \times 10^{11}/60$ s

$= 2.81 \times 10^9$ s^{-1}

At 10 °C min^{-1}, T_p=565.29 K,

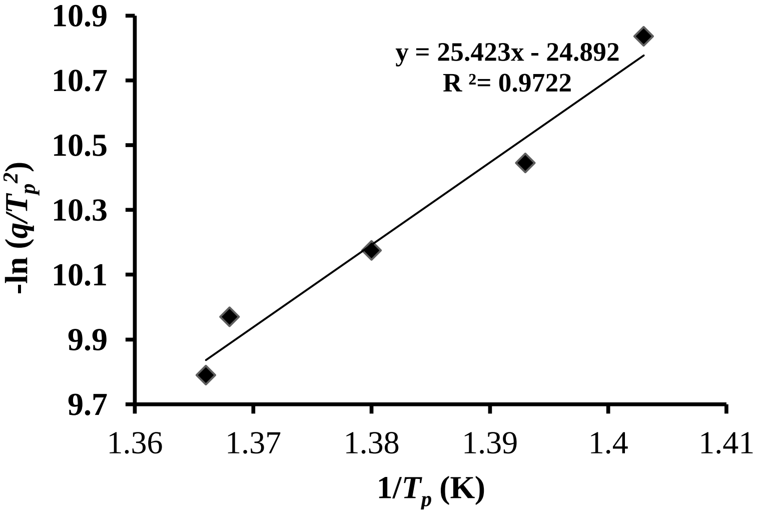
ΔS= 8.3143 J K^{-1} mol^{-1} x ln(2.81x10^9 s^{-1})(6.626x10^{-34} Js)/(1.3807x10^{-23} J K^{-1})(565.29 K)

= 8.3143 J K^{-1} mol^{-1} x ln(0.1349 x 1.769x10^{-3})

= -69.3 J K^{-1} mol^{-1}

I.14 Descriptions of calculations of E_d, A and ΔS for PVC/PHA$_{\text{SPKO-5}}$ during second stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	712.99	1.403	508354.7401	1.967	10.836
15	718.09	1.393	515653.2481	2.909	10.445
20	724.53	1.380	524943.7209	3.810	10.175
25	731.00	1.368	534361.0000	4.678	9.970
30	732.02	1.366	535853.2804	5.599	9.790



Equation for the Kissinger plot: Y = 25.423X – 24.892 (R^2 = 0.9722)

With gradient, E_d/R = 25.423 x 10^3 K

E_d= 25423 K x 8.3143 J K^{-1} mol^{-1}

= 211374.4489 J mol^{-1}

= 211.4 kJ mol^{-1}

With intersection of y-axis, $\ln(AR/E_d)$ = 24.892

$AR/E_d = e^{24.892}$

$A = E_d/R \times e^{24.892}$

= 25423 x $e^{24.892}$ min^{-1}

=1.64 x 10^{15} min^{-1}

=1.64 x 10^{15}/60 s

= 2.74 x 10^{13} s^{-1}

At 10 °C min^{-1}, T_p=712.99 K,

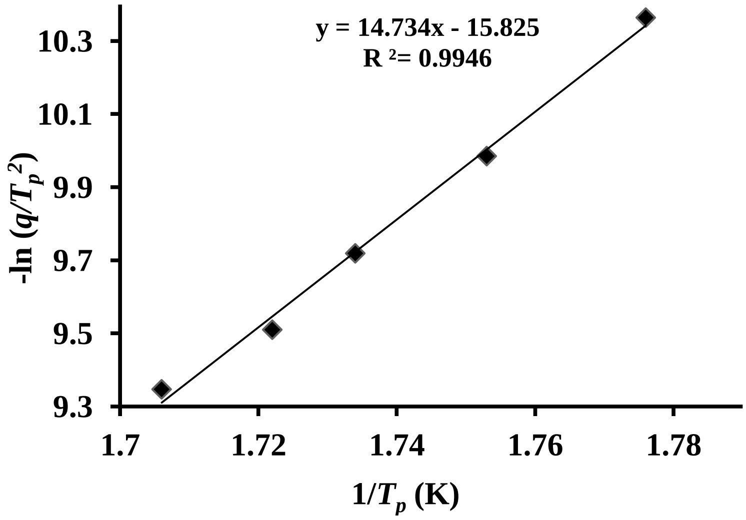
ΔS= 8.3143 J K^{-1} mol^{-1} x ln(2.74x10^{13} s^{-1})(6.626x10^{-34} Js)/(1.3807x10^{-23} J K^{-1})(712.99 K)

= 8.3143 J K^{-1} mol^{-1} x ln(1314.93 x 1.403x10^{-3})

= 5.09 J K^{-1} mol^{-1}

I.15 Descriptions of calculations of E_d, A and ΔS for PVC/degPHA$_{SPKO-2.5}$ during first stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	563.06	1.776	317036.5636	3.154	10.364
15	570.57	1.753	325550.1249	4.608	9.985
20	576.71	1.734	332594.4241	6.013	9.719
25	580.69	1.722	337200.8761	7.414	9.510
30	586.33	1.706	343782.8689	8.726	9.347



Equation for the Kissinger plot: Y = 14.734X – 15.825 (R^2 = 0.9946)

With gradient, E_d/R= 14.734 x 10^3 K

E_d = 14734 K x 8.3143 J K^{-1} mol^{-1}

= 122502.8962 J mol^{-1}

= 122.5 kJ mol^{-1}

With intersection of y-axis, $\ln(AR/E_d)$ = 15.825

$AR/E_d = e^{15.825}$

$A = E_d/R$ x $e^{15.825}$

= 14734 x $e^{15.825}$ min^{-1}

= 1.1 x 10^{11} min^{-1}

= 1.1 x 10^{11}/60 s

= 1.83 x 10^9 s^{-1}

At 10 ℃ min^{-1}, T_p=563.06 K,

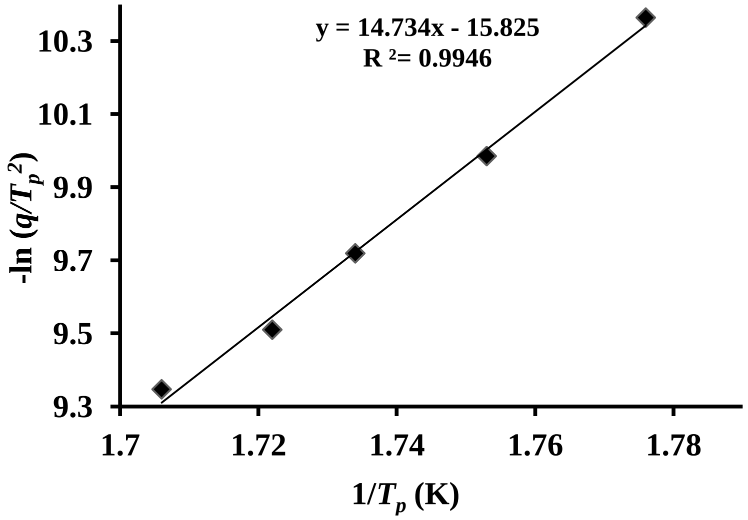
ΔS= 8.3143 J K^{-1} mol^{-1} x ln(1.83x10^9 s^{-1})(6.626x10^{-34} Js)/(1.3807x10^{-23} J K^{-1})(563.06 K)

= 8.3143 J K^{-1} mol^{-1} x ln(8.782x10^{-2} x 1.776x10^{-3})

= -72.9 J K^{-1} mol^{-1}

I.16 Descriptions of calculations of E_d, A and ΔS for PVC/degPHA$_{SPKO\text{-}2.5}$ during second stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	712.87	1.403	508183.6369	1.968	10.836
15	715.98	1.397	512627.3604	2.926	10.439
20	719.61	1.390	517838.5521	3.862	10.162
25	726.04	1.378	527134.0816	4.743	9.956
30	726.34	1.376	527569.7956	5.686	9.776



Equation for the Kissinger plot: Y = 34.509X – 37.693 (R^2 = 0.9416)

With gradient, E_d/R= 34.509 x 10^3 K

E_d = 34509 K x 8.3143 J K^{-1} mol^{-1}

= 286918.1787 J mol^{-1}

= 286.9 kJ mol^{-1}

With intersection of y-axis, $\ln(AR/E_d)$ = 37.693

$AR/E_d = e^{37.693}$

$A = E_d/R \times e^{37.693}$

= 34509 x $e^{37.693}$ min^{-1}

= 8.09 x 10^{20} min^{-1}

= 8.09 x 10^{20}/60 s

= 1.35 x 10^{19} s^{-1}

At 10 °C min^{-1}, T_p=712.87 K,

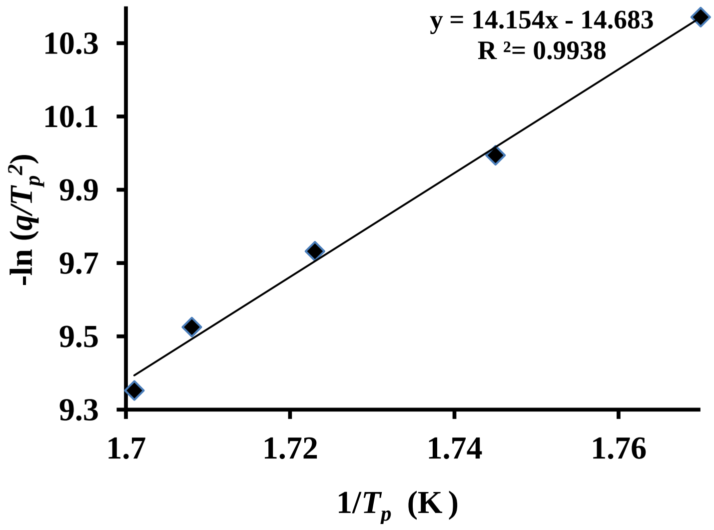
ΔS= 8.3143 J K^{-1} mol^{-1} x ln(1.35x10^{19} s^{-1})(6.626x10^{-34} Js)/(1.3807x10^{-23} J K^{-1})(712.87 K)

= 8.3143 J K^{-1} mol^{-1} x ln(6.48x10^{8} x 1.403x10^{-3})

= 114.1 J K^{-1} mol^{-1}

I.17 Descriptions of calculations of E_d, A and ΔS for PVC/degPHA$_{SPKO-5}$ during first stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	564.84	1.770	319044.2256	3.134	10.371
15	572.98	1.745	328306.0804	4.569	9.994
20	580.52	1.723	337003.4704	5.935	9.732
25	585.31	1.708	342587.7961	7.297	9.525
30	587.93	1.701	345661.6849	8.679	9.352



Equation for the Kissinger plot: Y = 14.154X – 14.683 (R^2 = 0.9938)

With gradient, E_d/R = 14.154 x 10^3 K

E_d= 14154 K x 8.3143 J K^{-1} mol^{-1}

= 117680.6022 J mol^{-1}

= 117.7 kJ mol^{-1}

With intersection of y-axis, $\ln(AR/E_d)$ = 14.683

$AR/E_d = e^{14.683}$

$A = E_d/R \times e^{14.683}$

= 14154 x $e^{14.683}$ min^{-1}

=3.37 x 10^{10} min^{-1}

=3.37 x 10^{10}/60 s

= 5.62 x 10^8 s^{-1}

At 10 °C min^{-1}, T_p=564.84 K,

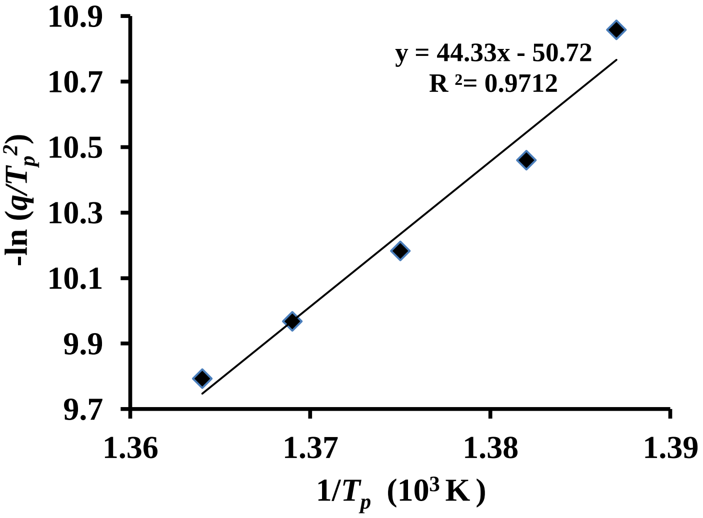
ΔS= 8.3143 J K^{-1} mol^{-1} x ln(5.62x10^8 s^{-1})(6.626x10^{-34} Js)/(1.3807x10^{-23} J K^{-1})(564.84 K)

= 8.3143 J K^{-1} mol^{-1} x ln(2.697x10^{-2} x 1.770x10^{-3})

= -82.7 J K^{-1} mol^{-1}

I.18 Descriptions of calculations of E_d, A and ΔS for PVC/degPHA$_{SPKO-5}$ during second stage of degradation

q (K min^{-1})	T_p (K)	$1/T_p$ (10^{-3} K^{-1})	T_p^2 (K^2)	q/T_p^2 (10^{-5} min^{-1} K^{-1})	$-\ln(q/T_p^2)$
10	720.76	1.387	519494.9776	1.925	10.858
15	723.54	1.382	523510.1316	2.865	10.460
20	727.38	1.375	529081.6644	3.780	10.183
25	730.30	1.369	533338.0900	4.687	9.968
30	733.03	1.364	537332.9809	5.583	9.793



Equation for the Kissinger plot: Y = 44.33X – 50.72 (R^2 = 0.9712)

With gradient, E_d/R = 44.33 x 10^3 K

E_d= 44330 K x 8.3143 J K^{-1} mol^{-1}

= 368572.919 J mol^{-1}

= 368.6 kJ mol^{-1}

With intersection of y-axis, $\ln(AR/E_d)$ = 50.72

AR/E_d = $e^{50.72}$

A = E_d/R x $e^{50.72}$

= 44330 x $e^{50.72}$ min^{-1}

=4.72 x 10^{26} min^{-1}

=4.72 x 10^{26}/60 s

= 7.87 x 10^{24} s^{-1}

At 10 °C min^{-1}, T_p=720.76 K,

ΔS= 8.3143 J K^{-1} mol^{-1} x ln(7.87x10^{24} s^{-1})(6.626x10^{-34} Js)/(1.3807x10^{-23} J K^{-1})(720.76 K)

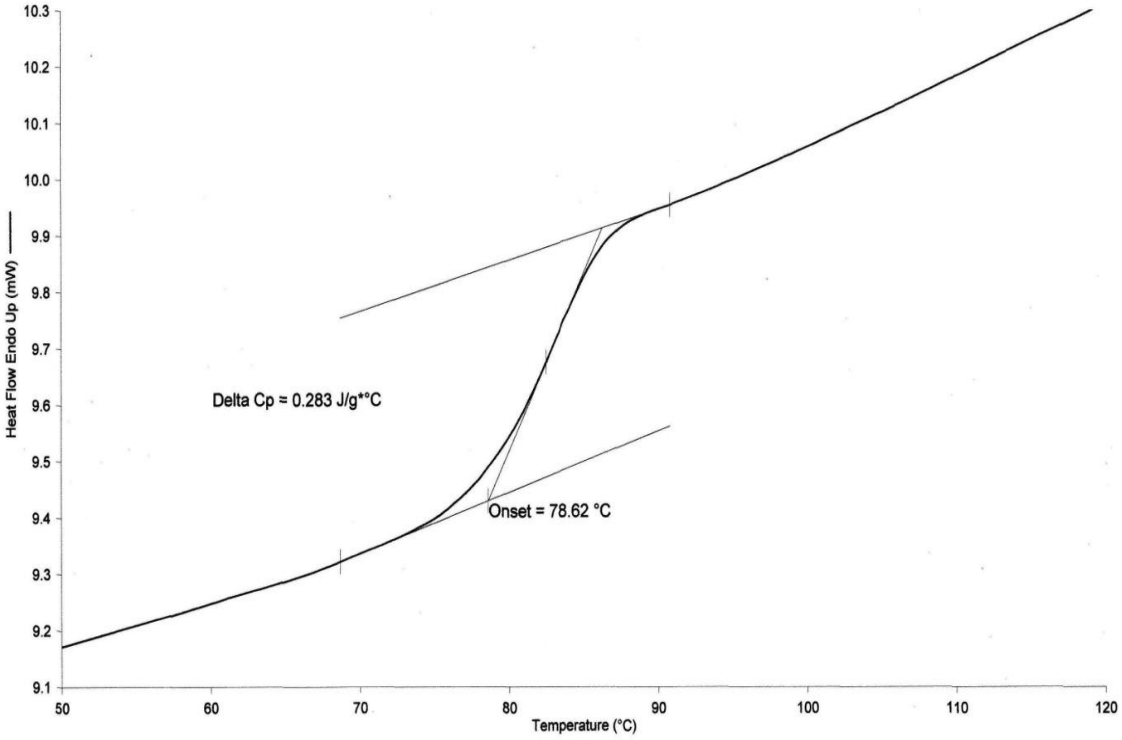
= 8.3143 J K^{-1} mol^{-1} x ln(3.777x10^{14} x 1.387x10^{-3})

= 224.4 J K^{-1} mol^{-1}

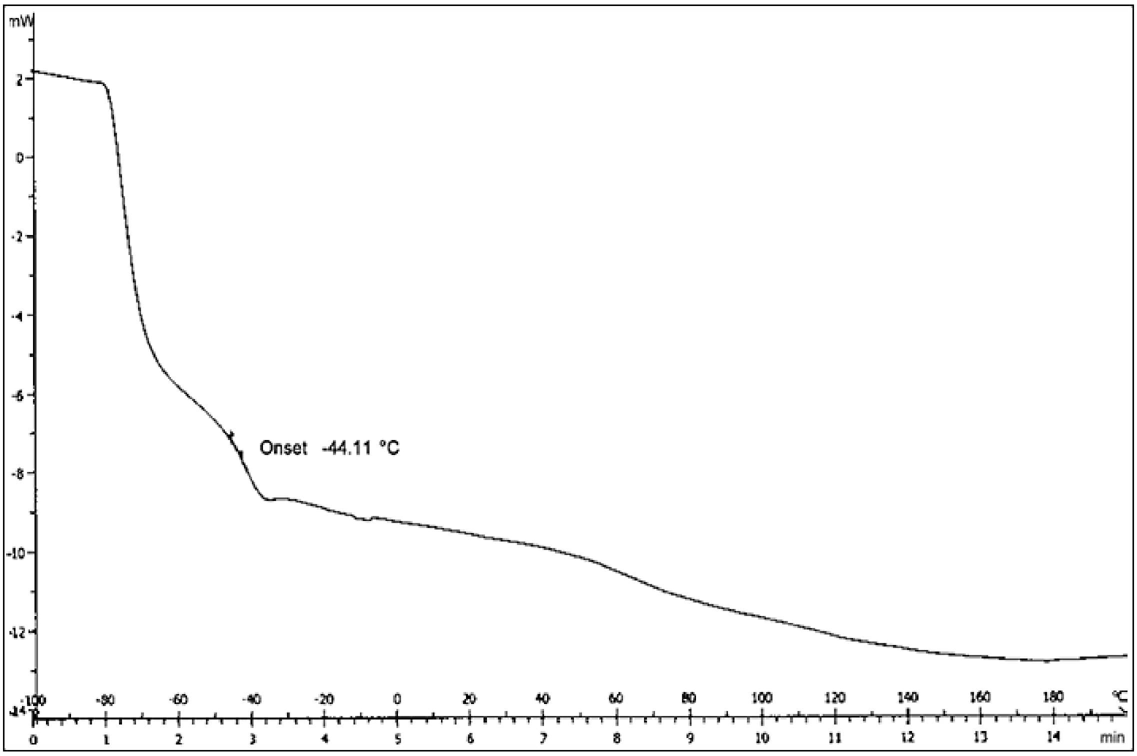
APPENDIX J:

DSC thermograms of PVC, PHA and PVC/PHA polymer blends

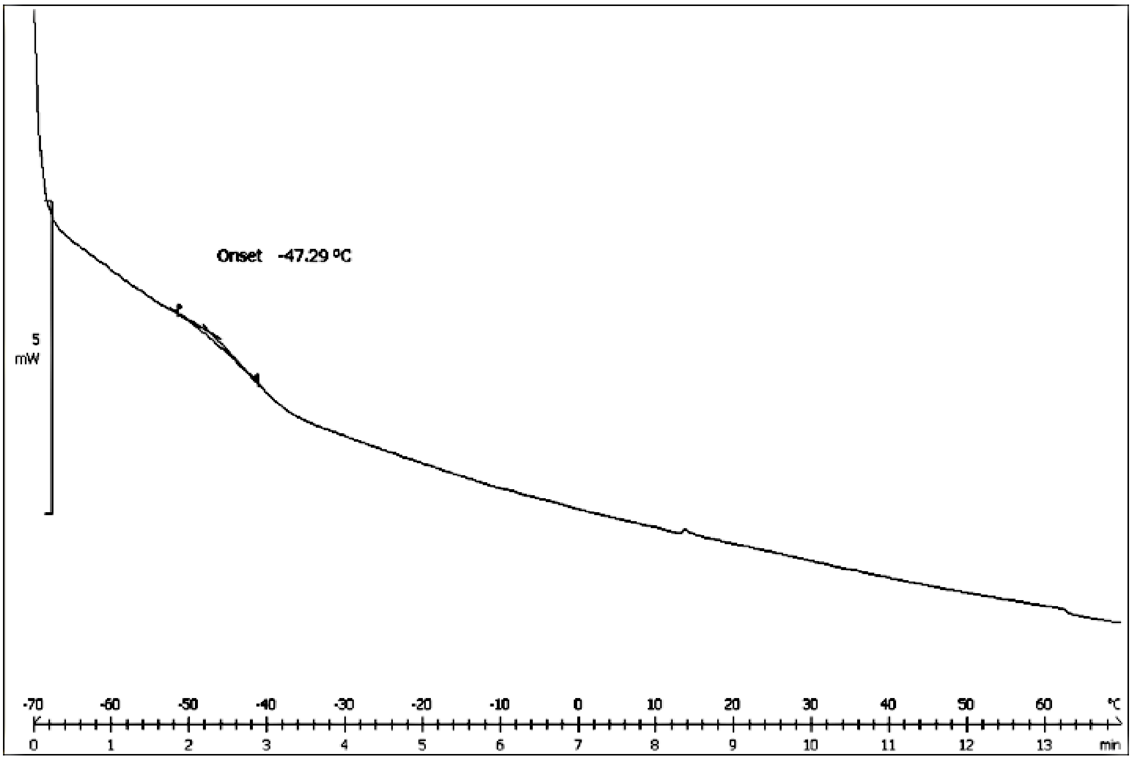
J.1 DSC thermogram of PVC



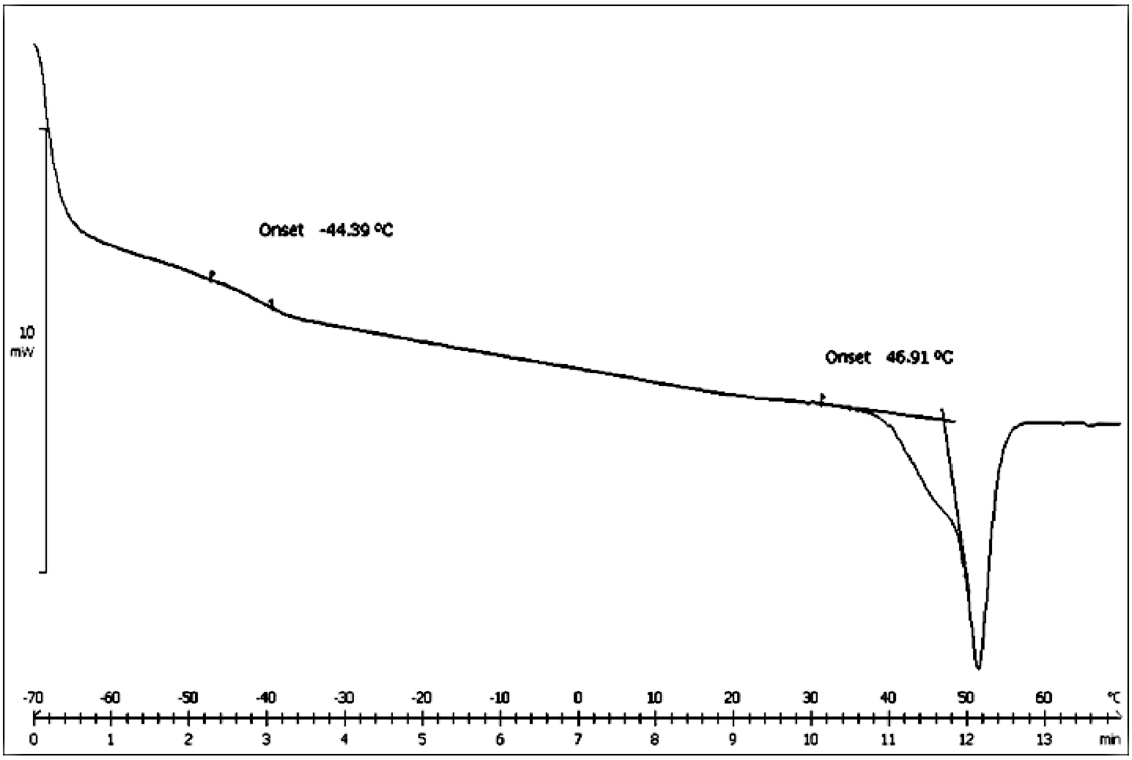
J.2 DSC thermogram of OA-derived PHA



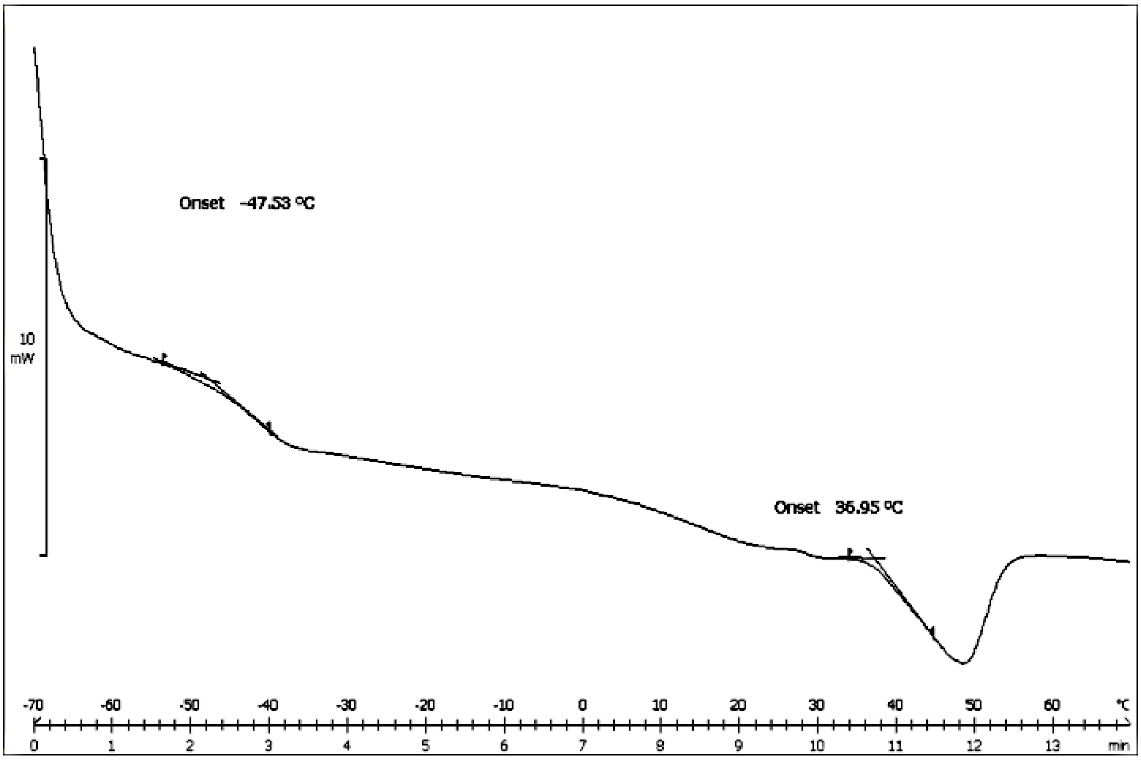
J.3 DSC thermogram of 170 ℃-treated OA-derived PHA



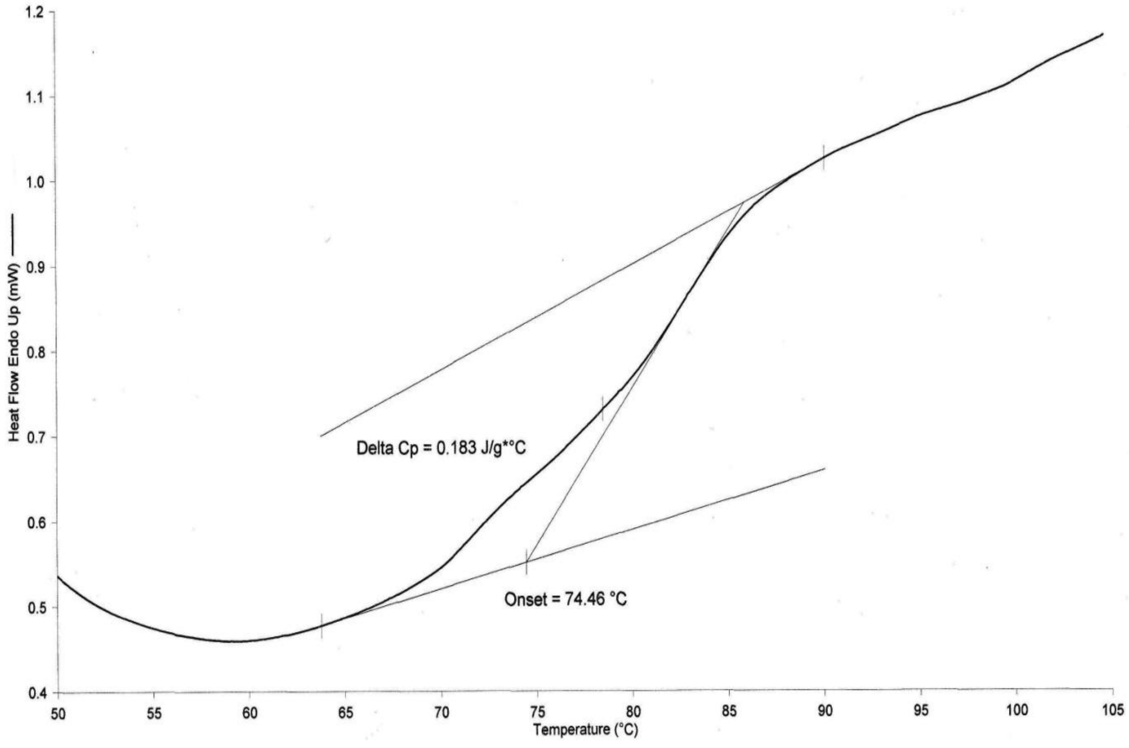
J.4 DSC thermogram of SPKO-derived PHA



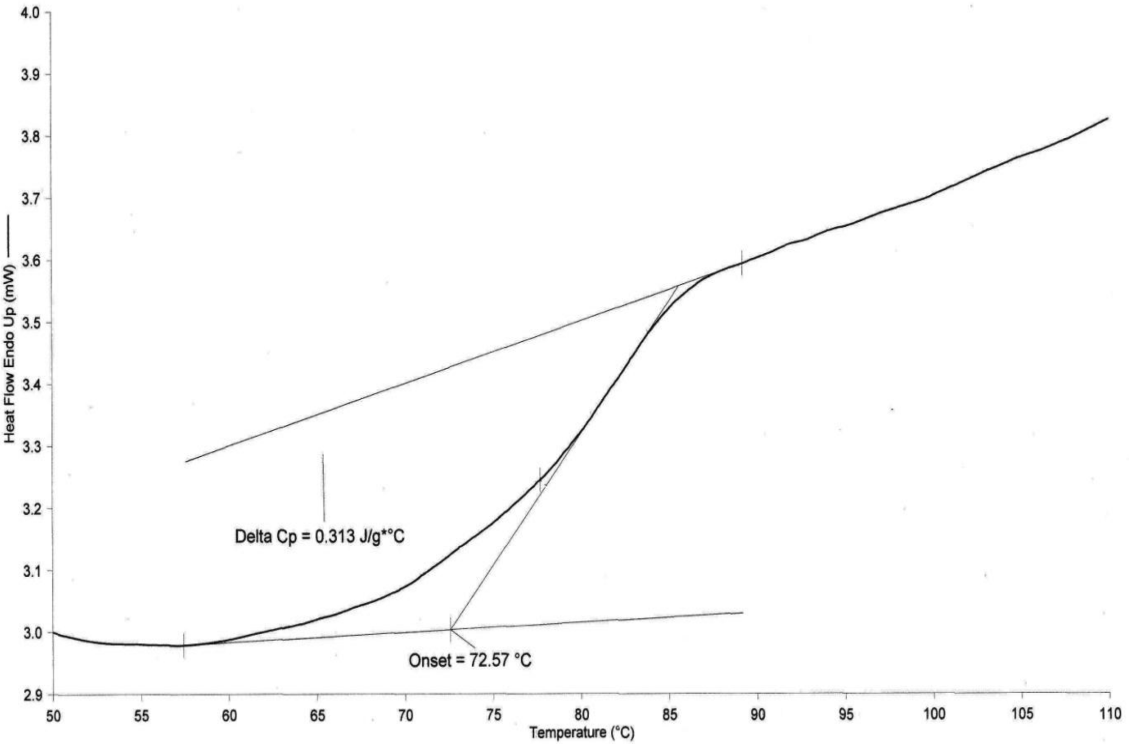
J.5 DSC thermogram of 170 ℃-treated SPKO-derived PH**A**



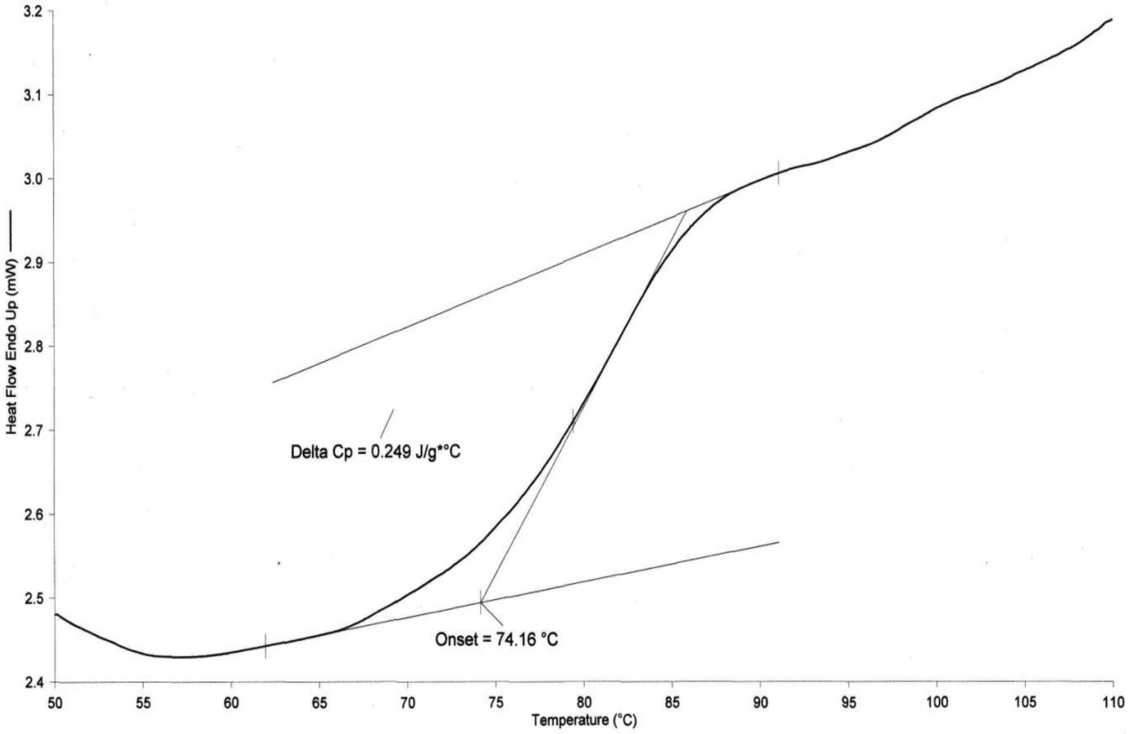
J.6 DSC thermogram of PVC/PHA$_{OA-2.5}$



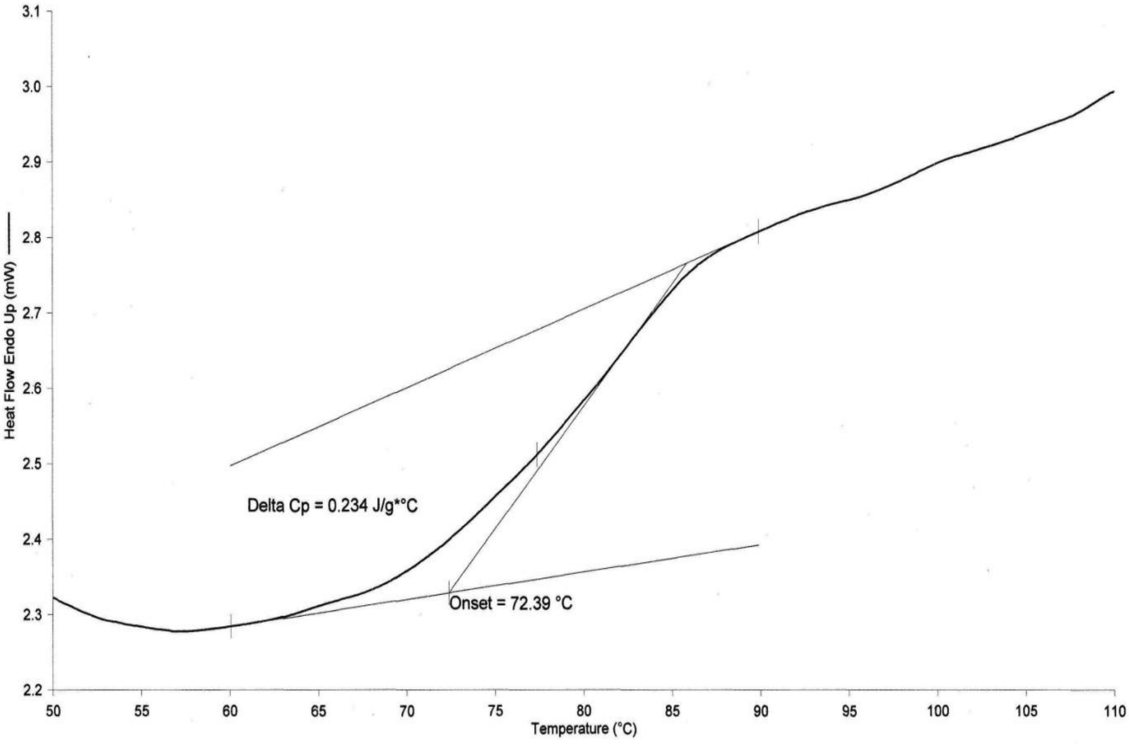
J.7 DSC thermogram of PVC/PHA$_{OA-5}$



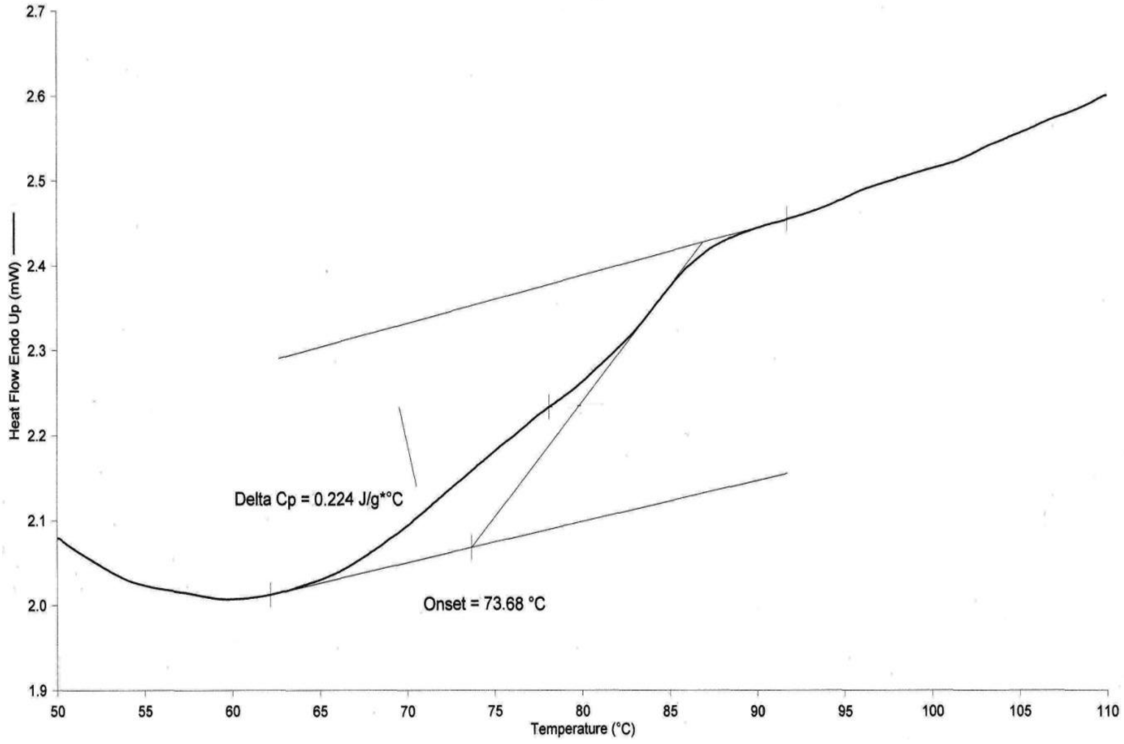
J.8 DSC thermogram of PVC/degPHA$_{OA-2.5}$



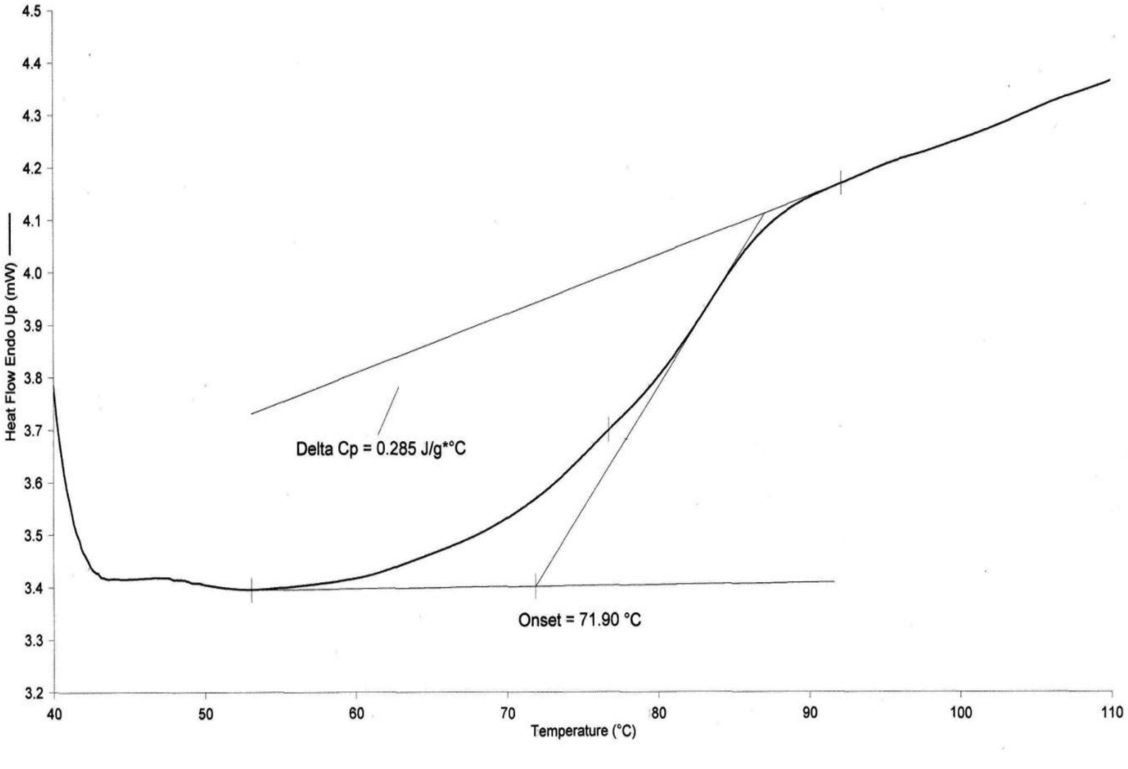
J.9 DSC thermogram of PVC/degPHA$_{OA-5}$



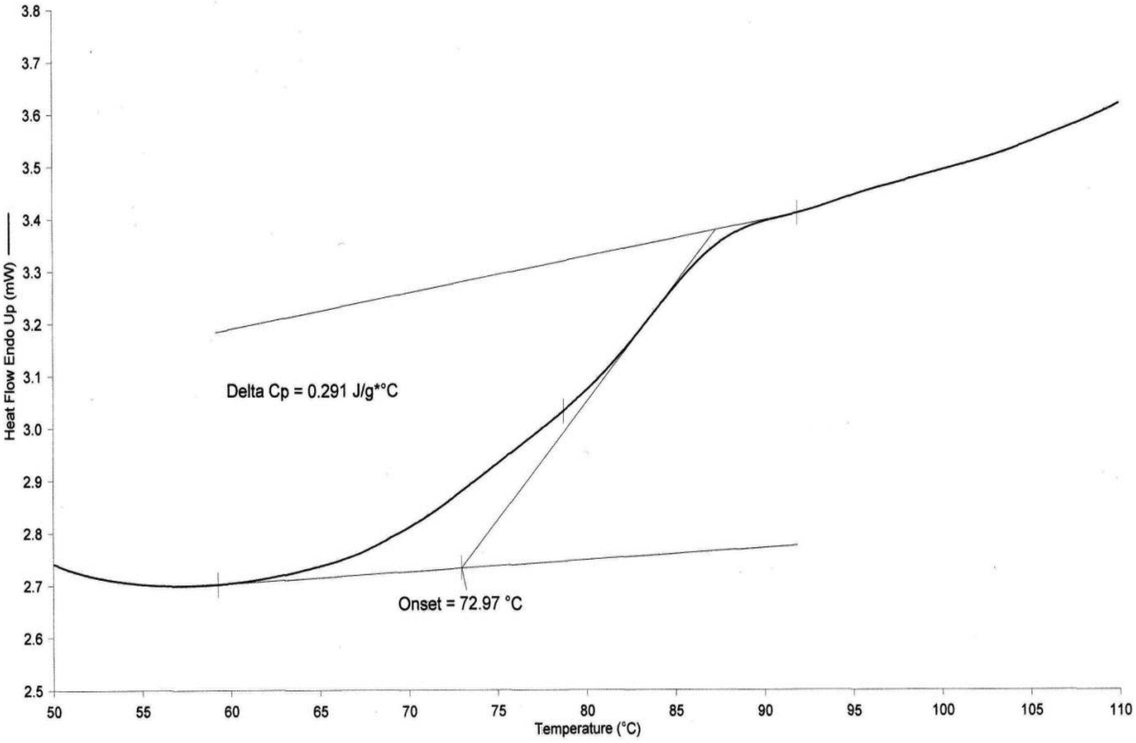
J.10 DSC thermogram of PVC/$PHA_{SPKO-2.5}$



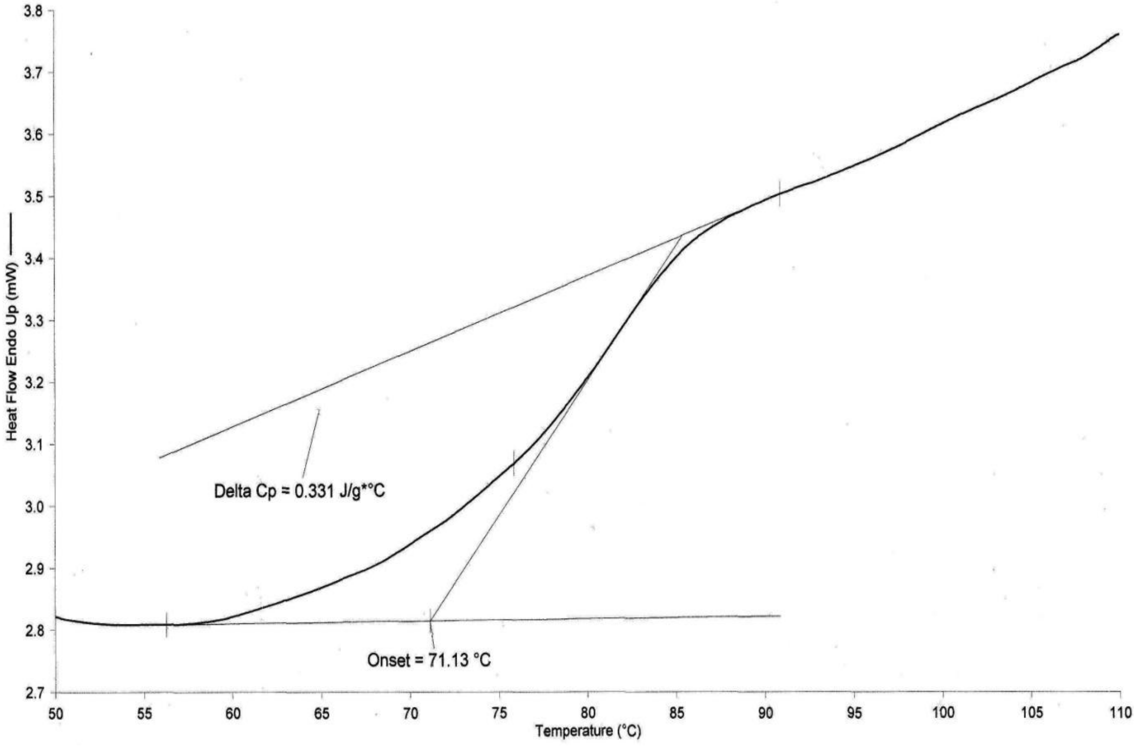
J.11 DSC thermogram of PVC/PHA_{SPKO-5}



J.12 DSC thermogram of PVC/degPHA$_{SPKO-2.5}$



J.13 DSC thermogram of PVC/degPHA$_{SPKO-5}$



Appendix K:

Determination of T_g for PVC/PHA polymer blends from Gordon-Taylor Equation

K.1 Calculation of T_g of PVC/PHA_{OA} through experimental T_g ($T_{g\ \text{exp}}$) substitution method

$T_{g\ \text{exp}}$ of PVC = 78.6 °C = 351.6 °K
$T_{g\ \text{exp}}$ of PHA_{OA} = -44.1 °C = 228.9 °K
$T_{g\ \text{exp}}$ of PVC/$\text{PHA}_{\text{OA-2.5}}$ = 74.5 °C = 347.5 °K
$T_{g\ \text{exp}}$ of PVC/$\text{PHA}_{\text{OA-5}}$ = 72.6 °C = 345.6 °K

W_{PHA} of PVC/$\text{PHA}_{\text{OA-2.5}}$ = 2.5/102.5 = 0.024
W_{PVC} of PVC/$\text{PHA}_{\text{OA-2.5}}$ = 100/102.5 = 0.976
W_{PHA} of PVC/$\text{PHA}_{\text{OA-5}}$ = 5/105 = 0.048
W_{PVC} of PVC/$\text{PHA}_{\text{OA-5}}$ = 100/105 = 0.952

Calculation of *k*-factor for PVC/$\text{PHA}_{\text{OA-2.5}}$:

$$T_g \text{ of PVC/PHA}_{\text{OA-2.5}} = (W_{\text{PHA}}\, T_{g\ \text{PHA}} + k\, W_{\text{PVC}}\, T_{g\ \text{PVC}}) / (W_{\text{PHA}} + k\, W_{\text{PVC}})$$

$$347.5\ ^{\circ}\text{K} = \frac{0.024\ (228.9\ ^{\circ}\text{K}) + k\ (0.976)\ (351.6\ ^{\circ}\text{K})}{0.024 + k\ (0.976)}$$

$$2.8464 = 4.0016\, k$$

$$k = 0.71$$

Calculation of *k*-factor for PVC/$\text{PHA}_{\text{OA-5}}$:

$$T_g \text{ of PVC/PHA}_{\text{OA-5}} = (W_{\text{PHA}}\, T_{g\ \text{PHA}} + k\, W_{\text{PVC}}\, T_{g\ \text{PVC}}) / (W_{\text{PHA}} + k\, W_{\text{PVC}})$$

$$345.6\ ^{\circ}\text{K} = \frac{0.048\ (228.9\ ^{\circ}\text{K}) + k\ (0.952)\ (351.6\ ^{\circ}\text{K})}{0.048 + k\ (0.952)}$$

$$5.6016 = 5.712\, k$$

$$k = 0.98$$

Average *k*-factor = (0.71+0.98)/2 = 0.85

$$\text{Calculated } T_g \text{ of PVC/PHA}_{\text{OA-2.5}} = \frac{0.024\ (228.9\ ^{\circ}\text{K}) + 0.85\ (0.976)\ (351.6\ ^{\circ}\text{K})}{0.024 + 0.85\ (0.976)}$$

$$= 348.1\ ^{\circ}\text{K}$$

$$= 75.1\ ^{\circ}\text{C}$$

$$\text{Calculated } T_g \text{ of PVC/PHA}_{\text{OA-5}} = \frac{0.048\ (228.9\ ^{\circ}\text{K}) + 0.85\ (0.952)\ (351.6\ ^{\circ}\text{K})}{0.048 + 0.85\ (0.952)}$$

$$= 344.7\ ^{\circ}\text{K}$$

$$= 71.7\ ^{\circ}\text{C}$$

K.2 Calculation of T_g of PVC/degPHA$_{OA}$ through experimental T_g substitution method

$T_{g\ \mathrm{exp}}$ of PVC = 78.6 °C = 351.6 °K
$T_{g\ \mathrm{exp}}$ of degPHA$_{OA}$ = -47.3 °C = 225.7 °K
$T_{g\ \mathrm{exp}}$ of PVC/degPHA$_{OA\text{-}2.5}$ = 74.2 °C = 347.2 °K
$T_{g\ \mathrm{exp}}$ of PVC/degPHA$_{OA\text{-}5}$ = 72.4 °C = 345.4 °K

W_{PHA} of PVC/degPHA$_{OA\text{-}2.5}$ = 2.5/102.5 = 0.024
W_{PVC} of PVC/degPHA$_{OA\text{-}2.5}$ = 100/102.5 = 0.976
W_{PHA} of PVC/degPHA$_{OA\text{-}5}$ = 5/105 = 0.048
W_{PVC} of PVC/degPHA$_{OA\text{-}5}$ = 100/105 = 0.952

Calculation of *k*-factor for PVC/degPHA$_{OA\text{-}2.5}$:

T_g of PVC/degPHA$_{OA\text{-}2.5}$ = $(W_{\mathrm{PHA}}\, T_{g\ \mathrm{PHA}} + k\, W_{\mathrm{PVC}}\, T_{g\ \mathrm{PVC}})/\ (W_{\mathrm{PHA}} + k\, W_{\mathrm{PVC}})$

$$347.2\ °\mathrm{K} = \frac{0.024\ (225.7\ °\mathrm{K}) + k\ (0.976)\ (351.6\ °\mathrm{K})}{0.024 + k\ (0.976)}$$

$$2.916 = 4.2944\, k$$

$$k = 0.68$$

Calculation of *k*-factor for PVC/degPHA$_{OA\text{-}5}$:

T_g of PVC/degPHA$_{OA\text{-}5}$ = $(W_{\mathrm{PHA}}\, T_{g\ \mathrm{PHA}} + k\, W_{\mathrm{PVC}}\, T_{g\ \mathrm{PVC}})/\ (W_{\mathrm{PHA}} + k\, W_{\mathrm{PVC}})$

$$345.4\ °\mathrm{K} = \frac{0.048\ (225.7\ °\mathrm{K}) + k\ (0.952)\ (351.6\ °\mathrm{K})}{0.048 + k\ (0.952)}$$

$$5.7456 = 5.9024\, k$$

$$k = 0.97$$

Average *k*-factor = (0.68+0.97)/2 = 0.83

Calculated T_g of PVC/degPHA$_{OA\text{-}2.5}$ $= \dfrac{0.024\ (225.7\ °\mathrm{K}) + 0.83\ (0.976)\ (351.6\ °\mathrm{K})}{0.024 + 0.83\ (0.976)}$

$$= 348.0\ °\mathrm{K}$$

$$= 75.0\ °\mathrm{C}$$

Calculated T_g of PVC/degPHA$_{OA\text{-}5}$ $= \dfrac{0.048\ (225.7\ °\mathrm{K}) + 0.83\ (0.952)\ (351.6\ °\mathrm{K})}{0.048 + 0.83\ (0.952)}$

$$= 344.4\ °\mathrm{K}$$

$$= 71.4\ °\mathrm{C}$$

K.3 Calculation of T_g of PVC/PHA$_{\text{SPKO}}$ through experimental T_g substitution method

$T_{g\text{ exp}}$ of PVC = 78.6 °C = 351.6 °K
$T_{g\text{ exp}}$ of PHA$_{\text{SPKO}}$ = -44.4 °C = 228.6 °K
$T_{g\text{ exp}}$ of PVC/PHA$_{\text{SPKO-2.5}}$ = 73.7 °C = 346.7 °K
$T_{g\text{ exp}}$ of PVC/PHA$_{\text{SPKO-5}}$ = 71.9 °C = 344.9 °K

W_{PHA} of PVC/PHA$_{\text{SPKO-2.5}}$ = 2.5/102.5 = 0.024
W_{PVC} of PVC/PHA$_{\text{SPKO-2.5}}$ = 100/102.5 = 0.976
W_{PHA} of PVC/PHA$_{\text{SPKO-5}}$ = 5/105 = 0.048
W_{PVC} of PVC/PHA$_{\text{SPKO-5}}$ = 100/105 = 0.952

Calculation of *k*-factor for PVC/PHA$_{\text{SPKO-2.5}}$:

$$T_g \text{ of PVC/PHA}_{\text{SPKO-2.5}} = (W_{\text{PHA}}\, T_{g\text{ PHA}} + k\, W_{\text{PVC}}\, T_{g\text{ PVC}}) / (W_{\text{PHA}} + k\, W_{\text{PVC}})$$

$$345.7\ ^\circ\text{K} = \frac{0.024\ (228.6\ ^\circ\text{K}) + k\ (0.976)\ (351.6\ ^\circ\text{K})}{0.024 + k\ (0.976)}$$

$$2.8344 = 4.7824\, k$$

$$k = 0.59$$

Calculation of *k*-factor for PVC/PHA$_{\text{SPKO-5}}$:

$$T_g \text{ of PVC/PHA}_{\text{SPKO-5}} = (W_{\text{PHA}}\, T_{g\text{ PHA}} + k\, W_{\text{PVC}}\, T_{g\text{ PVC}}) / (W_{\text{PHA}} + k\, W_{\text{PVC}})$$

$$344.9\ ^\circ\text{K} = \frac{0.048\ (228.6\ ^\circ\text{K}) + k\ (0.952)\ (351.6\ ^\circ\text{K})}{0.048 + k\ (0.952)}$$

$$5.5824 = 6.3784\, k$$

$$k = 0.88$$

Average *k*-factor = (0.59+0.88)/2 = 0.74

$$\text{Calculated } T_g \text{ of PVC/PHA}_{\text{SPKO-2.5}} = \frac{0.024\ (228.6\ ^\circ\text{K}) + 0.74\ (0.976)\ (351.6\ ^\circ\text{K})}{0.024 + 0.74\ (0.976)}$$

$$= 347.6\ ^\circ\text{K}$$

$$= 74.6\ ^\circ\text{C}$$

$$\text{Calculated } T_g \text{ of PVC/PHA}_{\text{SPKO-5}} = \frac{0.048\ (228.6\ ^\circ\text{K}) + 0.74\ (0.952)\ (351.6\ ^\circ\text{K})}{0.048 + 0.74\ (0.952)}$$

$$= 343.9\ ^\circ\text{K}$$

$$= 70.9\ ^\circ\text{C}$$

K.4 Calculation of T_g of PVC/degPHA$_{\mathrm{SPKO}}$ through experimental T_g substitution method

$T_{g\ \mathrm{exp}}$ of PVC = 78.6 °C = 351.6 °K
$T_{g\ \mathrm{exp}}$ of degPHA$_{\mathrm{SPKO}}$ = -47.5 °C = 225.5 °K
$T_{g\ \mathrm{exp}}$ of PVC/degPHA$_{\mathrm{SPKO\text{-}2.5}}$ = 73.0 °C = 346.0 °K
$T_{g\ \mathrm{exp}}$ of PVC/degPHA$_{\mathrm{SPKO\text{-}5}}$ = 71.1 °C = 344.1 °K

W_{PHA} of PVC/degPHA$_{\mathrm{SPKO\text{-}2.5}}$ = 2.5/102.5 = 0.024
W_{PVC} of PVC/degPHA$_{\mathrm{SPKO\text{-}2.5}}$ = 100/102.5 = 0.976
W_{PHA} of PVC/degPHA$_{\mathrm{SPKO\text{-}5}}$ = 5/105 = 0.048
W_{PVC} of PVC/degPHA$_{\mathrm{SPKO\text{-}5}}$ = 100/105 = 0.952

Calculation of k-factor for PVC/degSPKO$_{2.5}$:

$$T_g \text{ of PVC/degPHA}_{\mathrm{SPKO\text{-}2.5}} = (W_{\mathrm{PHA}}\, T_{g\ \mathrm{PHA}} + k\, W_{\mathrm{PVC}}\, T_{g\ \mathrm{PVC}}) / (W_{\mathrm{PHA}} + k\, W_{\mathrm{PVC}})$$

$$346.0\ ^\circ\mathrm{K} = \frac{0.024\ (225.5\ ^\circ\mathrm{K}) + k\ (0.976)\ (351.6\ ^\circ\mathrm{K})}{0.024 + k\ (0.976)}$$

$$2.892 = 5.4656\ k$$

$$k = 0.53$$

Calculation of k-factor for PVC/degSPKO$_5$:

$$T_g \text{ of PVC/degPHA}_{\mathrm{SPKO\text{-}5}} = (W_{\mathrm{PHA}}\, T_{g\ \mathrm{PHA}} + k\, W_{\mathrm{PVC}}\, T_{g\ \mathrm{PVC}}) / (W_{\mathrm{PHA}} + k\, W_{\mathrm{PVC}})$$

$$344.1\ ^\circ\mathrm{K} = \frac{0.048\ (225.5\ ^\circ\mathrm{K}) + k\ (0.952)\ (351.6\ ^\circ\mathrm{K})}{0.048 + k\ (0.952)}$$

$$5.6928 = 7.14\ k$$

$$k = 0.80$$

Average k-factor = (0.53+0.80)/2 = 0.67

$$\text{Calculated } T_g \text{ of PVC/degPHA}_{\mathrm{SPKO\text{-}2.5}} = \frac{0.024\ (225.5\ ^\circ\mathrm{K}) + 0.67\ (0.976)\ (351.6\ ^\circ\mathrm{K})}{0.024 + 0.67\ (0.976)}$$

$$= 347.1\ ^\circ\mathrm{K}$$

$$= 74.1\ ^\circ\mathrm{C}$$

$$\text{Calculated } T_g \text{ of PVC/degPHA}_{\mathrm{SPKO\text{-}5}} = \frac{0.048\ (225.5\ ^\circ\mathrm{K}) + 0.67\ (0.952)\ (351.6\ ^\circ\mathrm{K})}{0.048 + 0.67\ (0.952)}$$

$$= 342.8\ ^\circ\mathrm{K}$$

$$= 69.8\ ^\circ\mathrm{C}$$

K.5 Derivation of linear equations from Gordon-Taylor model, determination of the *k*-factor from the Polymath software and calculations of T_g for the polymer blends

Three linear equations with three different sets of w_{PHA} and w_{PVC} values were generated from the general equation as shown below, which was derived from the Gordon-Taylor equation:

$$T_g\, w_{\mathrm{PHA}} + T_g\, k\, w_{\mathrm{PVC}} - k\, w_{\mathrm{PVC}}\, T_{g\,\mathrm{PVC}} = w_{\mathrm{PHA}}\, T_{g\,\mathrm{PHA}}$$

where T_g, $T_g\, k$ and k are the variables; w_{PHA}, w_{PVC} and $w_{\mathrm{PVC}}\, T_{g\,\mathrm{PVC}}$ are the coefficients matrix; $w_{\mathrm{PHA}}\, T_{g\,\mathrm{PHA}}$ is the vector.

1) **For PVC/PHA$_{\mathbf{OA}}$,**
($T_{g\,\mathrm{PHA}} = 228.9$ K; $T_{g\,\mathrm{PVC}} = 351.6$ K)

Set 1: $w_{\mathrm{PHA}} = 0.23$; $w_{\mathrm{PVC}} = 0.77$
Eqn 1: $\mathbf{0.23}\boldsymbol{T_g} \mathbf{+ 0.77}\boldsymbol{T_g}\,\mathbf{k - 270.732k = 52.647}$ (1)

Set 2: $w_{\mathrm{PHA}} = 0.286$; $w_{\mathrm{PVC}} = 0.714$
Eqn 2: $\mathbf{0.286}\boldsymbol{T_g} \mathbf{+ 0.714}\boldsymbol{T_g}\,\mathbf{k - 251.0424k = 65.4654}$ (2)

Set 3: $w_{\mathrm{PHA}} = 0.333$; $w_{\mathrm{PVC}} = 0.667$
Eqn 3: $\mathbf{0.333}\boldsymbol{T_g} \mathbf{+ 0.667}\boldsymbol{T_g}\,\mathbf{k - 234.5172k = 76.2237}$ (3)

By solving the simultaneous equations of Eqn (1), (2) and (3) using Polymath software, the value of *k*-factor obtained was 0.91.

$$T_g \text{ of PVC/PHA}_{\mathrm{OA\text{-}2.5}} = \frac{0.024\,(228.9\ \mathrm{K}) + 0.91\,(0.976)\,(351.6\ \mathrm{K})}{0.024 + 0.91\,(0.976)}$$
$$= 348.4\ \mathrm{K}$$
$$= 75.4\ ^{\circ}\mathrm{C}$$

$$T_g \text{ of PVC/PHA}_{\mathrm{OA\text{-}5}} = \frac{0.048\,(228.9\ \mathrm{K}) + 0.91\,(0.952)\,(351.6\ \mathrm{K})}{0.048 + 0.91\,(0.952)}$$
$$= 345.2\ \mathrm{K}$$
$$= 72.2\ ^{\circ}\mathrm{C}$$

2) For PVC/degPHA$_{OA}$,

($T_{g\ PHA}$ = 225.7 K; $T_{g\ PVC}$ = 351.6 K)

Set 1: w_{PHA} = 0.35; w_{PVC} = 0.65

Eqn 1: $\mathbf{0.35T_g + 0.65T_g\,k - 228.54k = 78.995}$ (1)

Set 2: w_{PHA} = 0.474; w_{PVC} = 0.526

Eqn 2: $\mathbf{0.474T_g + 0.526T_g\,k - 184.9416k = 106.9818}$ (2)

Set 3: w_{PHA} = 0.55; w_{PVC} = 0.45

Eqn 3: $\mathbf{0.55T_g + 0.45T_g\,k - 158.22k = 124.135}$ (3)

By solving the simultaneous equations of Eqn (1), (2) and (3) using Polymath software, the value of *k*-factor obtained was 0.90.

$$T_g \text{ of PVC/degPHA}_{OA\text{-}2.5} = \frac{0.024\ (225.7\ \text{K}) + 0.90\ (0.976)\ (351.6\ \text{K})}{0.024 + 0.90\ (0.976)}$$

$$= 348.3\ \text{K}$$

$$= 75.3\ ^\circ\text{C}$$

$$T_g \text{ of PVC/degPHA}_{OA\text{-}5} = \frac{0.048\ (225.7\ \text{K}) + 0.90\ (0.952)\ (351.6\ \text{K})}{0.048 + 0.90\ (0.952)}$$

$$= 344.9\ \text{K}$$

$$= 71.9\ ^\circ\text{C}$$

3) For PVC/PHA$_{\mathrm{SPKO}}$,

($T_{g\ \mathrm{PHA}} = 228.6$ K; $T_{g\ \mathrm{PVC}} = 351.6$ K)

Set 1: $w_{\mathrm{PHA}} = 0.167$; $w_{\mathrm{PVC}} = 0.833$

Eqn 1: $\mathbf{0.167}\boldsymbol{T_g} + \mathbf{0.833}\boldsymbol{T_g}\ \mathbf{k - 292.8828k = 38.1762}$ (1)

Set 2: $w_{\mathrm{PHA}} = 0.333$; $w_{\mathrm{PVC}} = 0.667$

Eqn 2: $\mathbf{0.333}\boldsymbol{T_g} + \mathbf{0.667}\boldsymbol{T_g}\ \mathbf{k - 234.5172k = 76.1238}$ (2)

Set 3: $w_{\mathrm{PHA}} = 0.474$; $w_{\mathrm{PVC}} = 0.526$

Eqn 3: $\mathbf{0.474}\boldsymbol{T_g} + \mathbf{0.526}\boldsymbol{T_g}\ \mathbf{k - 184.9416k = 108.3564}$ (3)

By solving the simultaneous equations of Eqn (1), (2) and (3) using Polymath software, the value of *k*-factor obtained was 0.80.

$$T_g \text{ of PVC/PHA}_{\mathrm{SPKO\text{-}2.5}} = \frac{0.024\ (228.6\ ^\circ\mathrm{K}) + 0.80\ (0.976)\ (351.6\ ^\circ\mathrm{K})}{0.024 + 0.80\ (0.976)}$$

$$= 347.9\ ^\circ\mathrm{K}$$

$$= 74.9\ ^\circ\mathrm{C}$$

$$T_g \text{ of PVC/PHA}_{\mathrm{SPKO\text{-}5}} = \frac{0.048\ (228.6\ ^\circ\mathrm{K}) + 0.80\ (0.952)\ (351.6\ ^\circ\mathrm{K})}{0.048 + 0.80\ (0.952)}$$

$$= 344.3\ ^\circ\mathrm{K}$$

$$= 71.3\ ^\circ\mathrm{C}$$

4) For PVC/degPHA$_{\mathrm{SPKO}}$,

($T_{g\,\mathrm{PHA}} = 225.5$ K; $T_{g\,\mathrm{PVC}} = 351.6$ K)

Set 1: $w_{\mathrm{PHA}} = 0.3$; $w_{\mathrm{PVC}} = 0.7$

Eqn 1: $$\mathbf{0.3}\boldsymbol{T_g} + \mathbf{0.7}\boldsymbol{T_g}\,\mathbf{k} - \mathbf{246.12k} = \mathbf{67.65} \tag{1}$$

Set 2: $w_{\mathrm{PHA}} = 0.474$; $w_{\mathrm{PVC}} = 0.526$

Eqn 2: $$\mathbf{0.474}\boldsymbol{T_g} + \mathbf{0.526}\boldsymbol{T_g}\,\mathbf{k} - \mathbf{184.9416k} = \mathbf{106.887} \tag{2}$$

Set 3: $w_{\mathrm{PHA}} = 0.5$; $w_{\mathrm{PVC}} = 0.5$

Eqn 3: $$\mathbf{0.5}\boldsymbol{T_g} + \mathbf{0.5}\boldsymbol{T_g}\,\mathbf{k} - \mathbf{175.8k} = \mathbf{112.75} \tag{3}$$

By solving the simultaneous equations of Eqn (1), (2) and (3) using Polymath software, the value of *k*-factor obtained was 0.72.

$$\begin{aligned} T_g \text{ of PVC/degPHA}_{\mathrm{SPKO\text{-}2.5}} &= \frac{0.024\ (225.5\ ^\circ\mathrm{K}) + 0.72\ (0.976)\ (351.6\ ^\circ\mathrm{K})}{0.024 + 0.72\ (0.976)} \\ &= 347.4\ ^\circ\mathrm{K} \\ &= 74.4\ ^\circ\mathrm{C} \end{aligned}$$

$$\begin{aligned} T_g \text{ of PVC/degPHA}_{\mathrm{SPKO\text{-}5}} &= \frac{0.048\ (225.5\ ^\circ\mathrm{K}) + 0.72\ (0.952)\ (351.6\ ^\circ\mathrm{K})}{0.048 + 0.72\ (0.952)} \\ &= 343.3\ ^\circ\mathrm{K} \\ &= 70.3\ ^\circ\mathrm{C} \end{aligned}$$

Appendix L:

Determination of T_g, δT_g and ΔT_g for PVC/PHA polymer blends from Fox Equation

L.1 Calculation of T_g for PVC/PHA$_{OA\text{-}2.5}$

$T_{g\ \mathrm{exp}}$ of PHA$_{OA}$ = -44.1+273 K = 228.9 K;
$T_{g\ \mathrm{exp}}$ of PVC = 78.6+273 K = 351.6 K;
$T_{g\ \mathrm{exp}}$ of PVC/PHA$_{OA\text{-}2.5}$ = 74.5+273 K = 347.5 K

w_{PHA} = 2.5/102.5 = 0.024;
w_{PVC} = 100/102.5 = 0.976

$1/T_{g\ \mathrm{calc}} = (0.024/228.9) + (0.976/351.6)$
$= 2.881 \times 10^{-3}$
$T_{g\ \mathrm{calc}} = 347.1$ K
= 74.1 ℃

$\delta T_g = T_{g\ \mathrm{exp}} - T_{g\ \mathrm{calc}}$
= (74.5 - 74.1) ℃
= 0.4 ℃

$\Delta T_g = (T_{g\ \mathrm{exp}} - T_{g\ \mathrm{calc}} / T_{g\ \mathrm{pol}} - T_{g\ \mathrm{calc}}) \times 100$
= [(74.5 - 74.1)/(78.6-74.1)] x 100
= 8.9 %

L.2 Calculation of T_g for PVC/PHA$_{OA\text{-}5}$

$T_{g\ \mathrm{exp}}$ of PHA$_{OA}$ = -44.1+273 K = 228.9 K;
$T_{g\ \mathrm{exp}}$ of PVC = 78.6+273K = 351.6 K;
$T_{g\ \mathrm{exp}}$ of PVC/PHA$_{OA\text{-}5}$ = 72.6+273 K = 345.6 K

w_{PHA} = 5/105 = 0.048;
w_{PVC} = 100/105 = 0.952

$1/T_{g\ \mathrm{calc}} = (0.048/228.9) + (0.952/351.6)$
$= 2.917 \times 10^{-3}$
$T_{g\ \mathrm{calc}} = 342.8$ K
= 69.8 ℃

$\delta T_g = T_{g\ \mathrm{exp}} - T_{g\ \mathrm{calc}}$
= (72.6 - 69.8) ℃
= 2.8 ℃

$\Delta T_g = (T_{g\ \mathrm{exp}} - T_{g\ \mathrm{calc}} / T_{g\ \mathrm{pol}} - T_{g\ \mathrm{calc}}) \times 100$
= [(72.6 - 69.8)/(78.6-69.8)] x 100
= 31.8 %

L.3 Calculation of T_g for PVC/degPHA$_{\text{OA-2.5}}$

$T_{g\ \text{exp}}$ of degPHA$_{\text{OA-2.5}}$ = -47.3+273 K = 225.7 K;
$T_{g\ \text{exp}}$ of PVC = 78.6+273K = 351.6 K;
$T_{g\ \text{exp}}$ of PVC/degPHA$_{\text{OA-2.5}}$ = 74.2+273 K = 347.2 K

w_{PHA} = 2.5/102.5 = 0.024;
w_{PVC} = 100/102.5 = 0.976

$$1/T_{g\ \text{calc}} = (0.024/225.7) + (0.976/351.6) = 2.882 \times 10^{-3}$$
$$T_{g\ \text{calc}} = 347.0\ \text{K} = 74.0\ ^\circ\text{C}$$

$$\delta T_g = T_{g\ \text{exp}} - T_{g\ \text{calc}} = (74.2 - 74.0)\ ^\circ\text{C} = 0.2\ ^\circ\text{C}$$

$$\Delta T_g = (T_{g\ \text{exp}} - T_{g\ \text{calc}} / T_{g\ \text{pol}} - T_{g\ \text{calc}}) \times 100 = [(74.2 - 74.0)/(78.6-74.0)] \times 100 = 4.3\ \%$$

L.4 Calculation of T_g for PVC/degPHA$_{\text{OA-5}}$

$T_{g\ \text{exp}}$ of degPHA$_{\text{OA-5}}$ = -47.3+273 K = 225.7 K;
$T_{g\ \text{exp}}$ of PVC = 78.6+273K = 351.6 K;
$T_{g\ \text{exp}}$ of PVC/degPHA$_{\text{OA-5}}$ = 72.4+273 K = 345.4 K

w_{PHA} = 5/105 = 0.048;
w_{PVC} = 100/105 = 0.952

$$1/T_{g\ \text{calc}} = (0.048/225.7) + (0.952/351.6) = 2.919 \times 10^{-3}$$
$$T_{g\ \text{calc}} = 342.6\ \text{K} = 69.6\ ^\circ\text{C}$$

$$\delta T_g = T_{g\ \text{exp}} - T_{g\ \text{calc}} = (72.4 - 69.6)\ ^\circ\text{C} = 2.8\ ^\circ\text{C}$$

$$\Delta T_g = (T_{g\ \text{exp}} - T_{g\ \text{calc}} / T_{g\ \text{pol}} - T_{g\ \text{calc}}) \times 100 = [(72.4 - 69.6)/(78.6-69.6)] \times 100 = 31.1\ \%$$

L.5 Calculation of T_g for PVC/PHA$_{\text{SPKO-2.5}}$

$T_{g\text{ exp}}$ of PHA$_{\text{SPKO-2.5}}$ = -44.4+273 K = 228.6 K;
$T_{g\text{ exp}}$ of PVC = 78.6+273K = 351.6 K;
$T_{g\text{ exp}}$ of PVC/PHA$_{\text{SPKO-2.5}}$ = 73.7+273 K = 346.7 K

w_{PHA} = 2.5/102.5 = 0.024; w_{PVC} = 100/102.5 = 0.976

$1/T_{g\text{ calc}}$ = (0.024/228.6) + (0.976/351.6)
= 2.881 x 10^{-3}
$T_{g\text{ calc}}$ = 347.1 K
= 74.1 ℃

$\delta\ T_g = T_{g\text{ exp}} - T_{g\text{ calc}}$
= (73.7 - 74.1) ℃
= -0.4 ℃

$\Delta\ T_g = (T_{g\text{ exp}} - T_{g\text{ calc}} / T_{g\text{ pol}} - T_{g\text{ calc}})$ x 100
= [(73.7 - 74.1)/(78.6-74.1)] x 100
= -8.9 %

L.6 Calculation of T_g for PVC/PHA$_{\text{SPKO-5}}$

$T_{g\text{ exp}}$ of PHA$_{\text{SPKO-5}}$ = -44.4+273 K = 228.6 K;
$T_{g\text{ exp}}$ of PVC = 78.6+273K = 351.6 K;
$T_{g\text{ exp}}$ of PVC/PHA$_{\text{SPKO-5}}$ = 71.9+273 K = 344.9 K

w_{PHA} = 5/105 = 0.048;
w_{PVC} = 100/105 = 0.952

$1/T_{g\text{ calc}}$ = (0.048/228.6) + (0.952/351.6)
= 2.918 x 10^{-3}
$T_{g\text{ calc}}$ = 342.7 K
= 69.7 ℃

$\delta\ T_g = T_{g\text{ exp}} - T_{g\text{ calc}}$
= (71.9 - 69.7) ℃
= 2.2 ℃

$\Delta\ T_g = (T_{g\text{ exp}} - T_{g\text{ calc}} / T_{g\text{ pol}} - T_{g\text{ calc}})$ x 100
= [(71.9 - 69.7)/(78.6-69.7)] x 100
= 24.7 %

L.7 Calculation of T_g for PVC/degPHA$_{\mathrm{SPKO-2.5}}$

$T_{g\ \mathrm{exp}}$ of degPHA$_{\mathrm{SPKO-2.5}}$ = -47.5+273 K = 225.5 K;
$T_{g\ \mathrm{exp}}$ of PVC = 78.6+273K = 351.6 K;
$T_{g\ \mathrm{exp}}$ of PVC/degPHA$_{\mathrm{SPKO-2.5}}$ = 73.0+273 K = 346.0 K

w_{PHA} = 2.5/102.5 = 0.024;
w_{PVC} = 100/102.5 = 0.976

$$1/T_{g\ \mathrm{calc}} = (0.024/225.5) + (0.976/351.6)$$
$$= 2.882 \times 10^{-3}$$
$$T_{g\ \mathrm{calc}} = 346.9\ \mathrm{K}$$
$$= 73.9\ ^{\circ}\mathrm{C}$$

$$\delta T_g = T_{g\ \mathrm{exp}} - T_{g\ \mathrm{calc}}$$
$$= (73.0 - 73.9)\ ^{\circ}\mathrm{C}$$
$$= -0.9\ ^{\circ}\mathrm{C}$$

$$\Delta T_g = (T_{g\ \mathrm{exp}} - T_{g\ \mathrm{calc}} / T_{g\ \mathrm{pol}} - T_{g\ \mathrm{calc}}) \times 100$$
$$= [(73.0 - 73.9)/(78.6-73.9)] \times 100$$
$$= -19.1\ \%$$

L.8 Calculation of T_g for PVC/degPHA$_{\mathrm{SPKO-5}}$

$T_{g\ \mathrm{exp}}$ of degPHA$_{\mathrm{SPKO-5}}$ = -47.5+273 K = 225.5 K;
$T_{g\ \mathrm{exp}}$ of PVC = 78.6+273K = 351.6 K;
$T_{g\ \mathrm{exp}}$ of PVC/degPHA$_{\mathrm{SPKO-5}}$ = 71.1+273 K = 344.1 K

w_{PHA} = 5/105 = 0.048;
w_{PVC} = 100/105 = 0.952

$$1/T_{g\ \mathrm{calc}} = (0.048/225.5) + (0.952/351.6)$$
$$= 2.920 \times 10^{-3}$$
$$T_{g\ \mathrm{calc}} = 342.4\ \mathrm{K}$$
$$= 69.4\ ^{\circ}\mathrm{C}$$

$$\delta T_g = T_{g\ \mathrm{exp}} - T_{g\ \mathrm{calc}}$$
$$= (71.1 - 69.4)\ ^{\circ}\mathrm{C}$$
$$= 1.7\ ^{\circ}\mathrm{C}$$

$$\Delta T_g = (T_{g\ \mathrm{exp}} - T_{g\ \mathrm{calc}} / T_{g\ \mathrm{pol}} - T_{g\ \mathrm{calc}}) \times 100$$
$$= [(71.1 - 69.4)/(78.6-69.4)] \times 100$$
$$= 18.5\ \%$$

APPENDIX M:

Determination of elastic modulus for PVC and PVC/PHA polymer blends

M.1 Calculation of elastic modulus for PVC

PVC film dimensions: 30.0000 x 6.2500 x 0.3000 mm

At 40.13 °C, $E = \dfrac{244826 \text{ Nm}^{-1} \text{ x } 3.0 \text{ cm}}{0.625 \text{ x } 0.03 \text{ cm}^2}$

$= \dfrac{3.92 \text{ x } 10^7 \text{ N}}{10^2 \text{ cm}^2}$

$= 3.92 \text{ GNm}^{-2}$

= 3.92 GPa

M.2 Calculation of elastic modulus for PVC/PHA$_{\text{OA-2.5}}$

PVC/PHA$_{\text{OA-2.5}}$ film dimensions: 30.0000 x 7.9500 x 0.2800 mm

At 39.93 °C, $E = \dfrac{272653 \text{ Nm}^{-1} \text{ x } 3.0 \text{ cm}}{0.795 \text{ x } 0.028 \text{ cm}^2}$

$= \dfrac{3.67 \text{ x } 10^7 \text{ N}}{10^2 \text{ cm}^2}$

$= 3.67 \text{ GNm}^{-2}$

= 3.67 GPa

M.3 Calculation of elastic modulus for PVC/PHA$_{\text{OA-5}}$

PVC/PHA$_{\text{OA-5}}$ film dimensions: 30.0000 x 7.2200 x 0.2900 mm

At 40.03 °C, $E = \dfrac{182254 \text{ Nm}^{-1} \text{ x } 3.0 \text{ cm}}{0.722 \text{ x } 0.029 \text{ cm}^2}$

$= \dfrac{2.61 \text{ x } 10^7 \text{ N}}{10^2 \text{ cm}^2}$

$= 2.61 \text{ GNm}^{-2}$

= 2.61 GPa

M.4 Calculation of elastic modulus for PVC/degPHA$_{\text{OA-2.5}}$

PVC/degPHA$_{\text{OA-2.5}}$ film dimensions: 30.0000 x 6.9300 x 0.2500 mm

At 40.06 °C, $E = \frac{164629\ \text{Nm}^{-1} \text{ x } 3.0\ \text{cm}}{0.693 \text{ x } 0.025\ \text{cm}^2}$

$= \frac{2.85 \text{ x } 10^7\ \text{N}}{10^2\ \text{cm}^2}$

$= 2.85\ \text{GNm}^{-2}$
$= 2.85\ \text{GPa}$

M.5 Calculation of elastic modulus for PVC/degPHA$_{\text{OA-5}}$

PVC/degPHA$_{\text{OA-5}}$ film dimensions: 30.0000 x 5.1300 x 0.5200 mm

At 40.13 °C, $E = \frac{186924\ \text{Nm}^{-1} \text{ x } 3.0\ \text{cm}}{0.513 \text{ x } 0.052\ \text{cm}^2}$

$= \frac{2.10 \text{ x } 10^7\ \text{N}}{10^2\ \text{cm}^2}$

$= 2.10\ \text{GNm}^{-2}$
$= 2.10\ \text{GPa}$

M.6 Calculation of elastic modulus for PVC/PHA$_{\text{SPKO-2.5}}$

PVC/PHA$_{\text{SPKO-2.5}}$ film dimensions: 30.0000 x 4.4300 x 0.2700 mm

At 40.09 °C, $E = \frac{129931\ \text{Nm}^{-1} \text{ x } 3.0\ \text{cm}}{0.443 \text{ x } 0.027\ \text{cm}^2}$

$= \frac{3.26 \text{ x } 10^7\ \text{N}}{10^2\ \text{cm}^2}$

$= 3.26\ \text{GNm}^{-2}$
$= 3.26\ \text{GPa}$

M.7 Calculation of elastic modulus for PVC/PHA$_{SPKO-5}$

PVC/PHA$_{SPKO-5}$ film dimensions: 30.0000 x 5.0900 x 0.2400 mm

At 39.84 °C, $E = \frac{70221 \text{ Nm}^{-1} \text{ x } 3.0 \text{ cm}}{0.509 \text{ x } 0.024 \text{ cm}^2}$

$= \frac{1.72 \text{ x } 10^7 \text{ N}}{10^2 \text{ cm}^2}$

$= 1.72 \text{ GNm}^{-2}$

$= 1.72$ GPa

M.8 Calculation of elastic modulus for PVC/degPHA$_{SPKO-2.5}$

PVC/degPHA$_{SPKO-2.5}$ film dimensions: 30.0000 x 9.8000 x 0.2900 mm

At 40.09 °C, $E = \frac{184016 \text{ Nm}^{-1} \text{ x } 3.0 \text{ cm}}{0.98 \text{ x } 0.029 \text{ cm}^2}$

$= \frac{1.94 \text{ x } 10^7 \text{ N}}{10^2 \text{ cm}^2}$

$= 1.94 \text{ GNm}^{-2}$

$= 1.94$ GPa

M.9 Calculation of elastic modulus for PVC/degPHA$_{SPKO-5}$

PVC/degPHA$_{SPKO-5}$ film dimensions: 30.0000 x 7.8000 x 0.3500 mm

At 40.08 °C, $E = \frac{135278 \text{ Nm}^{-1} \text{ x } 3.0 \text{ cm}}{0.78 \text{ x } 0.035 \text{ cm}^2}$

$= \frac{1.49 \text{ x } 10^7 \text{ N}}{10^2 \text{ cm}^2}$

$= 1.49 \text{ GNm}^{-2}$

$= 1.49$ GPa

APPENDIX N

PUBLICATIONS AND PRESENTATIONS

N.1 Publications

1. Sin MC, Gan SN, Annuar MSM, Tan IKP (2010) Thermodegradation of medium-chain-length poly(3-hydroxyalkanoates) produced by *Pseudomonas putida* from oleic acid. *Polymer Degradation & Stability* 95:2334-2342 (***ISI-Cited Publication***)

2. Sin MC, Tan IKP, Annuar MSM, Gan SN (2011) Characterization of oligomeric hydroxyalkanoic acids from thermal decomposition of palm kernel oil based biopolyester. *International Journal of Polymer Analysis and Characterization* 16(5): 337-347 (***ISI-Cited Publication****)*

3. Sin MC, Gan SN, Annuar MSM, Tan IKP (2011) Chain cleavage mechanism of palm kernel oil derived medium-chain-length poly(3-hydroxyalkanoates) during high temperature decomposition. *Polymer Degradation & Stability* 96: 1705-1710 ***(ISI-Cited Publication)***

4. Sin MC, Tan IKP, Annuar MSM, Gan SN (2012) Kinetics of thermodegradation of palm kernel oil derived medium-chain-length polyhydroxyalkanoates. *Journal of Applied Polymer Science. doi: 10.1002/app.38033* ***(ISI-cited publication)***

5. Sin MC, Tan IKP, Annuar MSM, Gan SN (2012) Thermal behavior and thermodegradation kinetics of poly(vinyl chloride) plasticized with polymeric and oligomeric medium-chain-length poly(3-hydroxyalkanoates). *Polymer Degradation and Stability* **(*Submitted; ISI-cited publication*)**

6. Sin MC, Tan IKP, Annuar MSM, Gan SN. (2012) Morphological, spectroscopic and mechanical characterization of lightly plasticized poly(vinyl chloride) with low and high molecular weight poly(3-hydroxyalkanoates). *European Polymer Journal* **(*Submitted; ISI-cited publication*)**

N.2 Oral Presentations

1. Sin MC, Gan SN, Annuar MSM, Tan IKP (2009) Thermodegradation of medium-chain-length poly(3-hydroxyalkanoates) produced by *Pseudomonas putida* from oleic acid. The 14th Biological Sciences Graduate Congress (14th BSGC), 10-12th of December 2009, Chulalongkorn University, Bangkok, Thailand.

2. Sin MC, Gan SN, Annuar MSM, Tan IKP (2010) Production of low molecular weight polyhydroxyalkanoates from medium-chain-length polyhydroxyalkanoates derived from saponified palm kernel oil. The 2nd International Conference on Natural Polymers (2nd ICNP) , 24-26th of September 2010, Institute of Macromolecular Science and Technology, Kottayam, Kerala, India. ***(Invited speaker)***

3. Sin MC, Gan SN, Annuar MSM, Tan IKP (2011) Medium-chain-length polyhydroxyalkanoates as eco-friendly plasticizer for poly(vinyl chloride). The 12th Association of Pacific Rim Universities, Doctorate Students Conference (12th APRU DSC), 4-7th of July 2011, Beijing, China. (***Best paper award)***

4. Sin MC, Gan SN, Annuar MSM, Tan IKP (2011) Plasticizing effect of low molecular weight medium-chain-length polyhydroxyalkanoates (mcl-PHA) on the PVC/mcl-PHA binary blends. The 3rd Asian Biomaterial Congress (3rd ABMC), 15-17th of September 2011, BEXCO, Busan, South Korea.

5. Sin MC, Gan SN, Annuar MSM, Tan IKP (2011) Assessment of poly(3-hydroxyalkanoates) and its oligoesters as natural based plasticizers for poly(vinyl chloride). The 7th Mathematics and Physical Sciences Graduate Congress (7th MPSGC), 12-14th of December 2011, National University of Singapore, Singapore.

N.3 Poster Presentations

1. Sin MC, Gan SN, Annuar MSM, Tan IKP (2009) A study of the chain cleavage mechanism for the thermal degradation of oleic acid derived medium-chain-length poly(3-hydroxyalkanoates). The 2nd International Conference on Bio-based Polymers (2nd ICBP), 11-13th of November 2009, University Sains Malaysia, Penang, Malaysia.

2. Sin MC, Gan SN, Annuar MSM, Tan IKP (2010) Thermal degradation of microbial polyesters, medium-chain-length polyhydroxyalkanoates (mcl-PHA), derived from renewable resources such as oleic acid and palm kernel oil. The Innovation and Creativity Expo, 1-3rd of April, 2010, University of Malaya, Kuala Lumpur, Malaysia. (***Gold Medal Award***)

3. Sin MC, Gan SN, Annuar MSM, Tan IKP (2011) Bacterial polyhydroxyalkanoates as an eco-friendly plasticizer for polyvinylchloride (PVC). Malaysia Technology Expo (MTE), 17-19th of February 2011, Kuala Lumpur Exhibition Centre, Malaysia.