Characterization of Bark Derived PF Resin from Mountain-Pine Beetle Infested Lodgepole Pine

Yong Zhao[+], Ning Yan[+], Martin Feng[*]

[+] **University of Toronto**

[*] **FPInnovations-Forintek**

Outline

- **Introduction**
- **Methodology**
- **Results**
- **Conclusions**
- **Acknowledgement**

Introduction

Bark Materials

- Waste residue used as hog fuel or dispose without recovery
- Low heating value
- Renewable biomass, low carbon footprints
- No impact on human and animal feed system
- Similarity in composition to wood, except extractives, polyphenol, and suberin
- Good Candidate for higher value applications

Adhesive Application of Biomass

- **Lignin, bark, bark extractives as a replacement of petroleum-based phenol to synthesize PF resins**
- **Feasibility demonstrated in previous studies**
- **Inconsistency in performance due to low reactivity and high variability in structures**
- **Chemical modification e.g. liquefaction or phenolation**

…However,

- **Curing behavior & curing kinetics**
- **Bark from Beetle infested trees**

Beetle Infestation

- **Mountain Pine Beetle (*Dendroctonus ponderosae Hopkins*)**

Sources:British Columbia Ministry of Forests and Range/L. Maclaughlan

Chemical Composition of Barks

%	Beetle-Infested Pine Bark	Non-infested Pine Bark
Ethanol-Toluene extractives	17.7 (0.5)	18.2 (0.4)
Dicholormethane extractives	14.2 (0.5)	14.7 (0.8)
Hot water soluble *	7.5 (1.2)	3.9 (1.2)
1% NaOH solubles	68.1 (0.5)	61.9 (0.3)
Holocellulose	46.7 (1.2)	46.5 (0.4)
α -cellulose	20.5 (1.1)	24.9 (3.2)
Klason lignin	42.6 (0.7)	45.1 (0.6)
Ash	4.0 (1.8)	4.1 (2.8)

*** After Ethanol-Toluene extraction. Number in bracket is standard deviation.**

Beetle Infestation

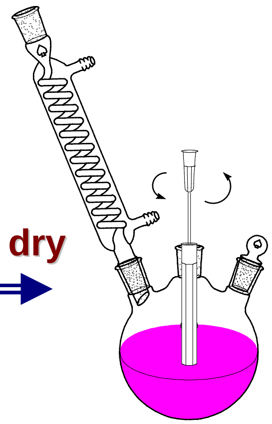
- **Mountain Pine Beetle (*Dendroctonus ponderosae Hopkins*)**
- **Change in chemical composition, physical and mechanical properties after infestation**
- **Suitability of application after beetle infestation is unknown**

Methodology

Bark powder (BI, GP)

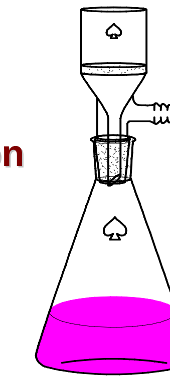
Oven dry

Phenolation



Phase separation

Residue filtered by Whattman Millipore.



Adhesive synthesis and Characterization (TGA, DSC, Lap-shear test)

BI: Mountain Pine Beetle infested lodgepole pine bark; GP: Non-infested lodgepole pine bark

Adhesive Synthesis

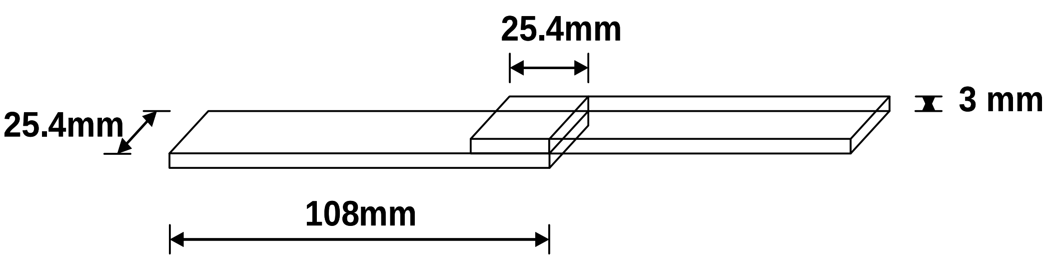
- **Liquefied lodgepole pine bark (150℃, Solvent/bark=3, 120min, 3%catalyst)**
- **Formaldehyde (37%)**
- **Sodium hydroxide (40%, 1/3 of total weight)**
- **Reaction temperature 65 ℃, kept for 10 min**
- **2/3 of NaOH was added and reaction temperature increased to 85 ℃ kept for 60min**
- **Lab PF and commercial PF as comparison.**

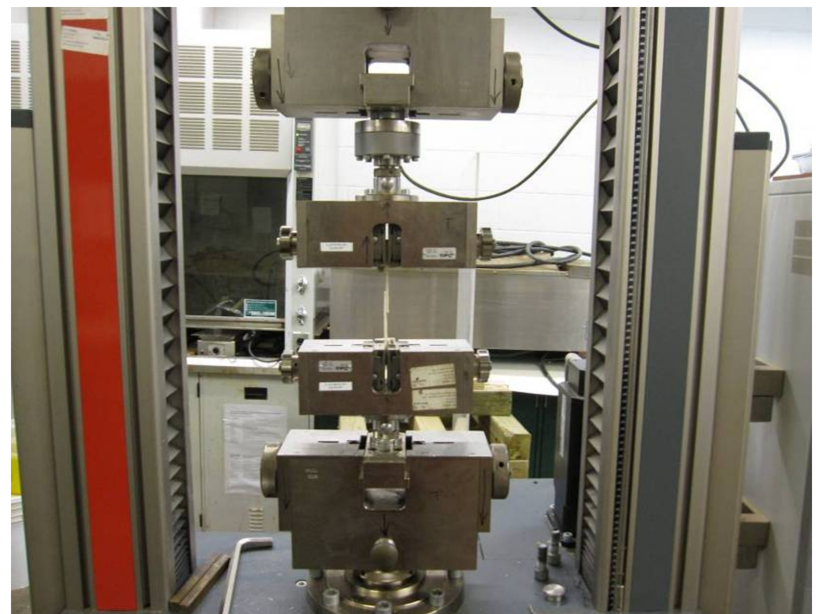
Adhesive Characterization

- **Mw, Mn and Mw/Mn were measured by MALDI/TOF/TOF.**
- **Dynamic DSC scans were made with the heating rates of 5℃/min,10 ℃/min, 15 ℃/min, 20 ℃/min, respectively.**
- **Kissinger method was applied to calculated the activation energy.**
- **Isothermal DSC scans were made at 110 ℃, 120 ℃, 130 ℃, 140 ℃, 150 ℃, respectively.**
- **TGA of cured resins with heating rate of 10 ℃/min, from room temperature to 700 ℃, N_2 atmosphere.**

Adhesive Characterization

- **Bondability-Lap shear Tests**
  - **Poplar veneer: 3 mm thickness**
  - **Resin solid: 0.025~0.035g/cm²**
  - **Hot press condition: 160℃, 4.5mm thickness control, 3min.**
  - **Zwick universal test machine at 1.3 mm/min crosshead speed.**
  - **Dry test, Water-soak-and-dry test, boiling water test.**





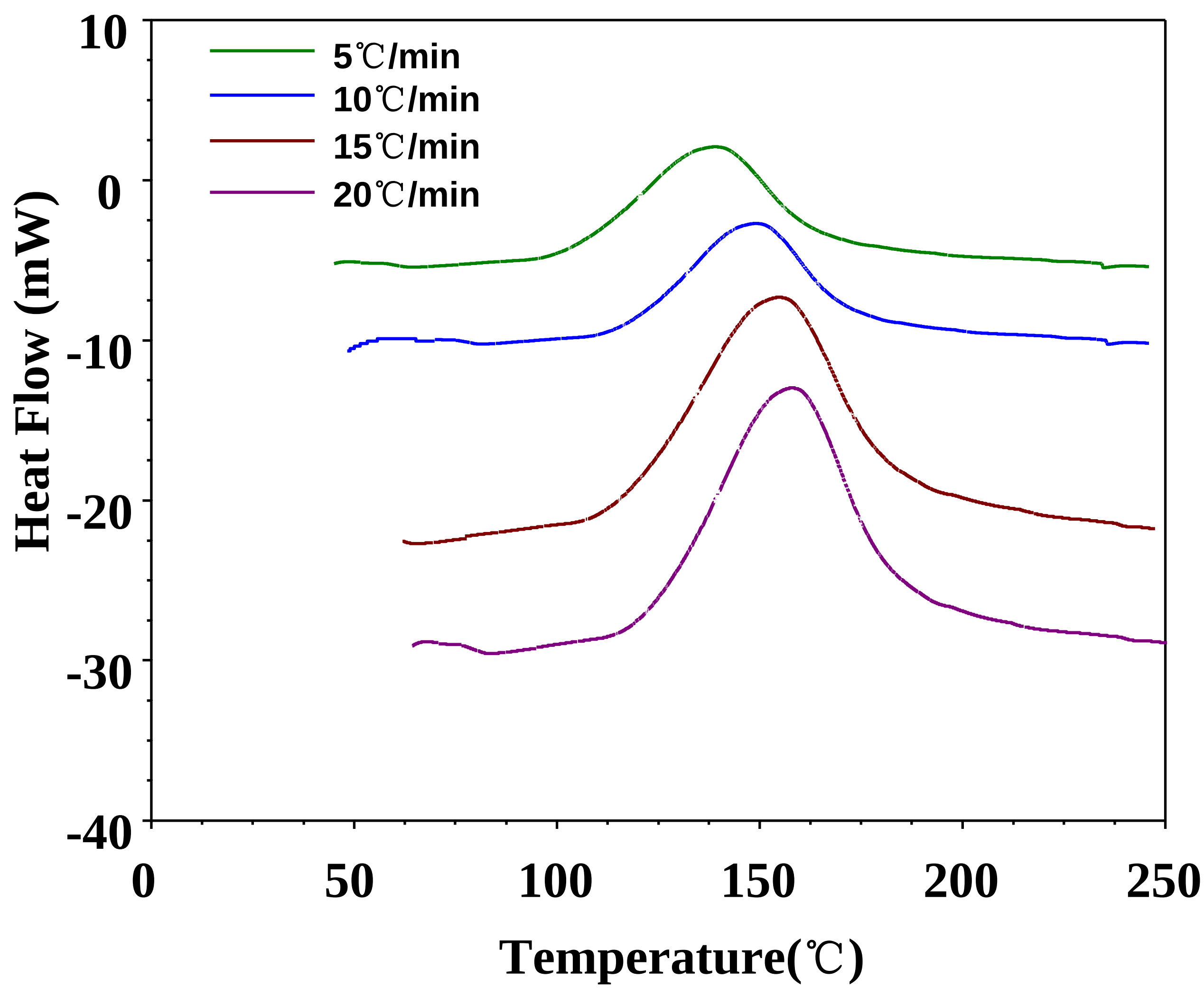
Results

Properties of the resins

	pH	Solids content (%)	Viscosity (cps)	Gel time at 120℃ (s)	Mn (Da)	Mw (Da)	Mw/Mn
Commercial PF	11.16	59.0	200	172	212.09	386.48	1.82
LBI PF	12.07	52.97	125	152	325.57	619.49	1.89
LGP PF	11.96	52.35	150	161	437.17	849.24	1.95
Lab PF	11.93	48.87	25	173	258.95	327.27	1.25

LBI PF: Liquefied mountain pine beetle infested pine bark PF resin;
LGP PF: Liquefied green pine bark PF resin

Dynamic DSC curve of bark-derived PF resin (non infested)

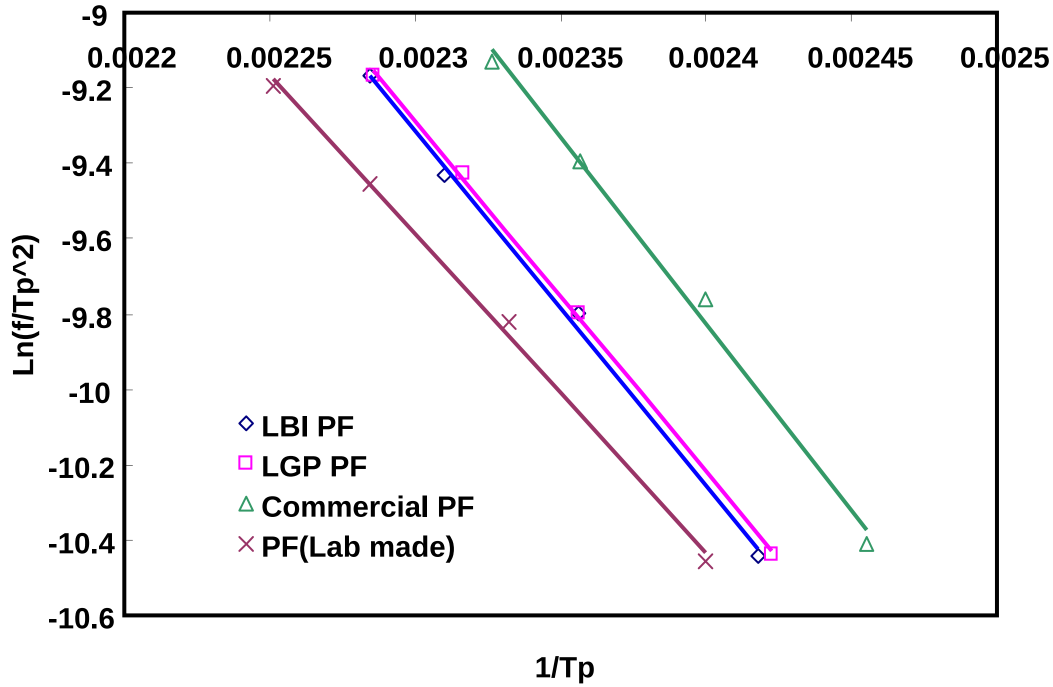


Exo Up

Resin Cure Temperatures

Heating rate (℃/min)	LBI PF Onset Temp (℃)	LBI PF Peak Temp (℃)	LGP PF Onset Temp (℃)	LGP PF Peak Temp (℃)	Commercial PF Onset Temp (℃)	Commercial PF Peak Temp (℃)	PF (Lab made) Onset Temp (℃)	PF (Lab made) Peak Temp (℃)
0 *	98.86	133.93	99.34	133.29	98.11	127.76	95.86	136.00
5	103.66	140.57	104.9	139.81	105.54	134.35	103.89	143.74
10	113.43	151.45	113.66	151.47	113.94	143.66	112.53	155.74
15	117.97	159.89	119.38	158.67	122.21	151.35	120.66	164.79
20	123.03	164.73	124.78	164.51	128.81	156.85	128.6	171.23

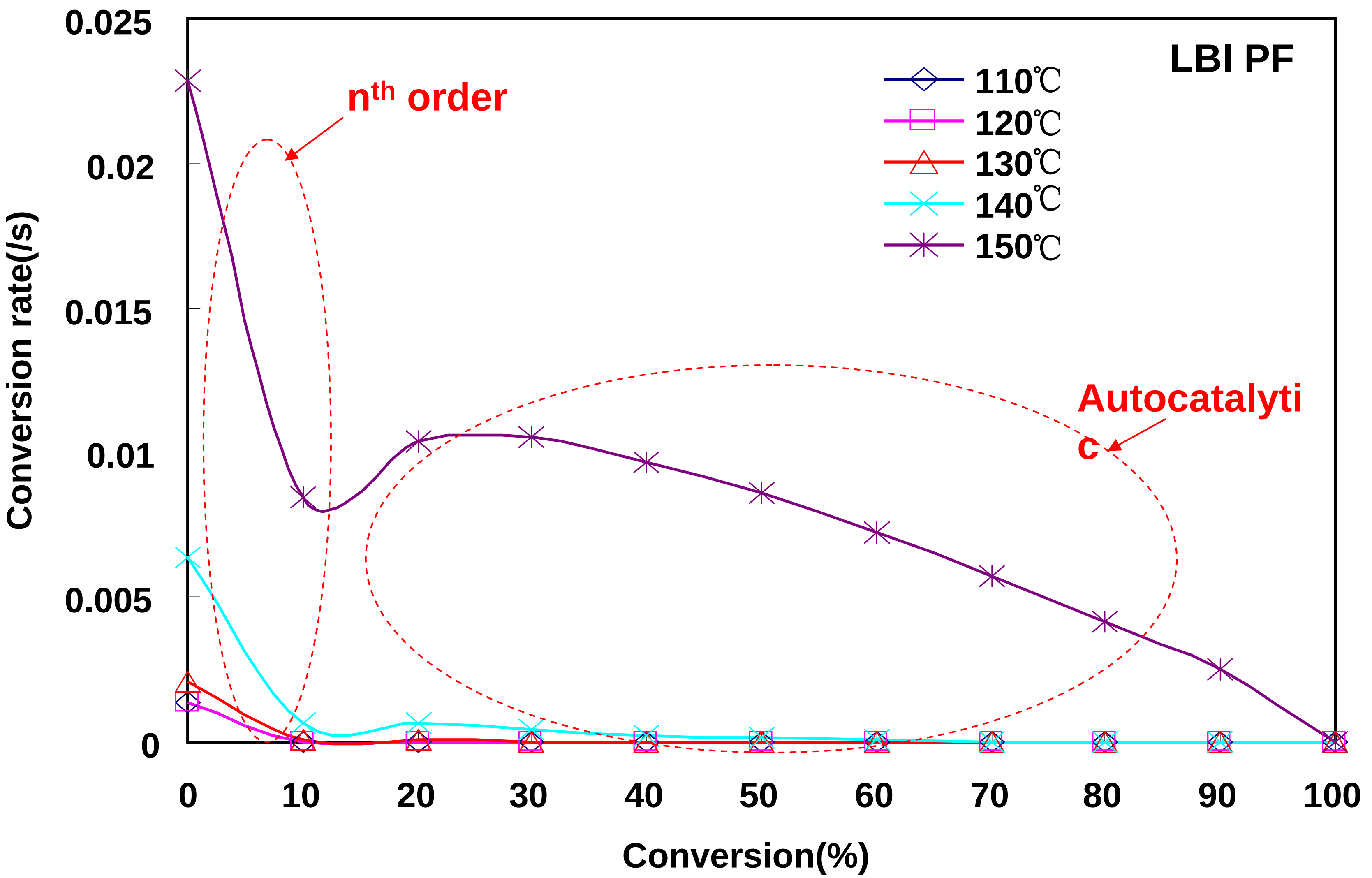
*** Extrapolated values from the intercept of the plots of the onset temperatures and peak temperatures versus the heating rate.**

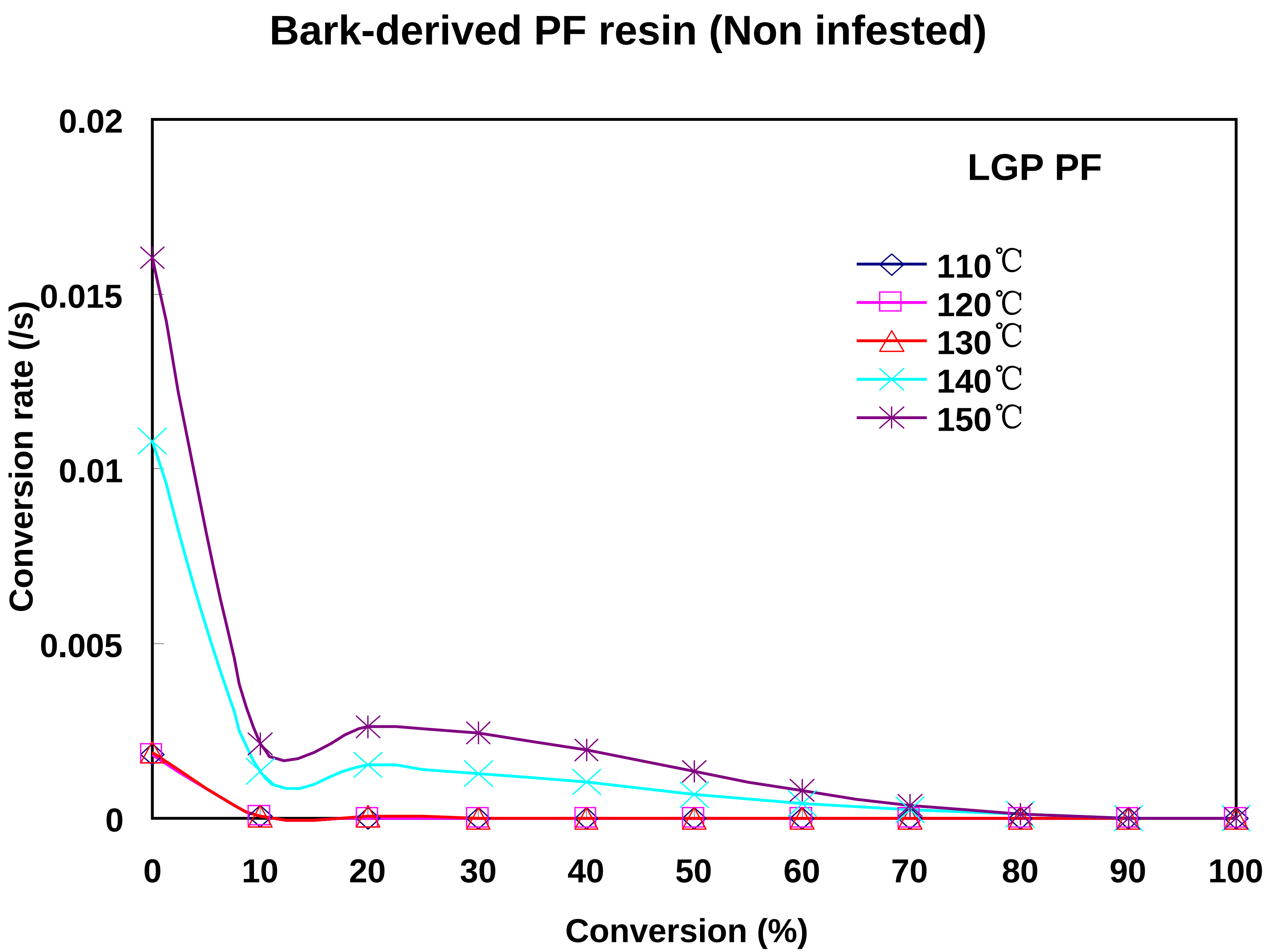


	E (kJ/mol)	A (s^{-1})	Kinetic Equation	r
LBI PF	*78.12*	*2.08X10⁹* → 2.08×10^{9}	$\frac{d\alpha}{dt} = 2.08\times10^{9}\exp(-\frac{9400}{T})(1-\alpha)^{0.84}$	*0.99*
LGP PF	*77.60*	1.85×10^{9}	$\frac{d\alpha}{dt} = 1.85\times10^{9}\exp(-\frac{9338}{T})(1-\alpha)^{0.75}$	*0.99*
PF (Lab)	*70.22*	1.59×10^{8}	$\frac{d\alpha}{dt} = 1.59\times10^{8}\exp(-\frac{8450}{T})(1-\alpha)^{0.64}$	*0.99*
COM PF	*82.23*	1.18×10^{10}	$\frac{d\alpha}{dt} = 1.18\times10^{10}\exp(-\frac{9895}{T})(1-\alpha)^{0.56}$	*0.99*

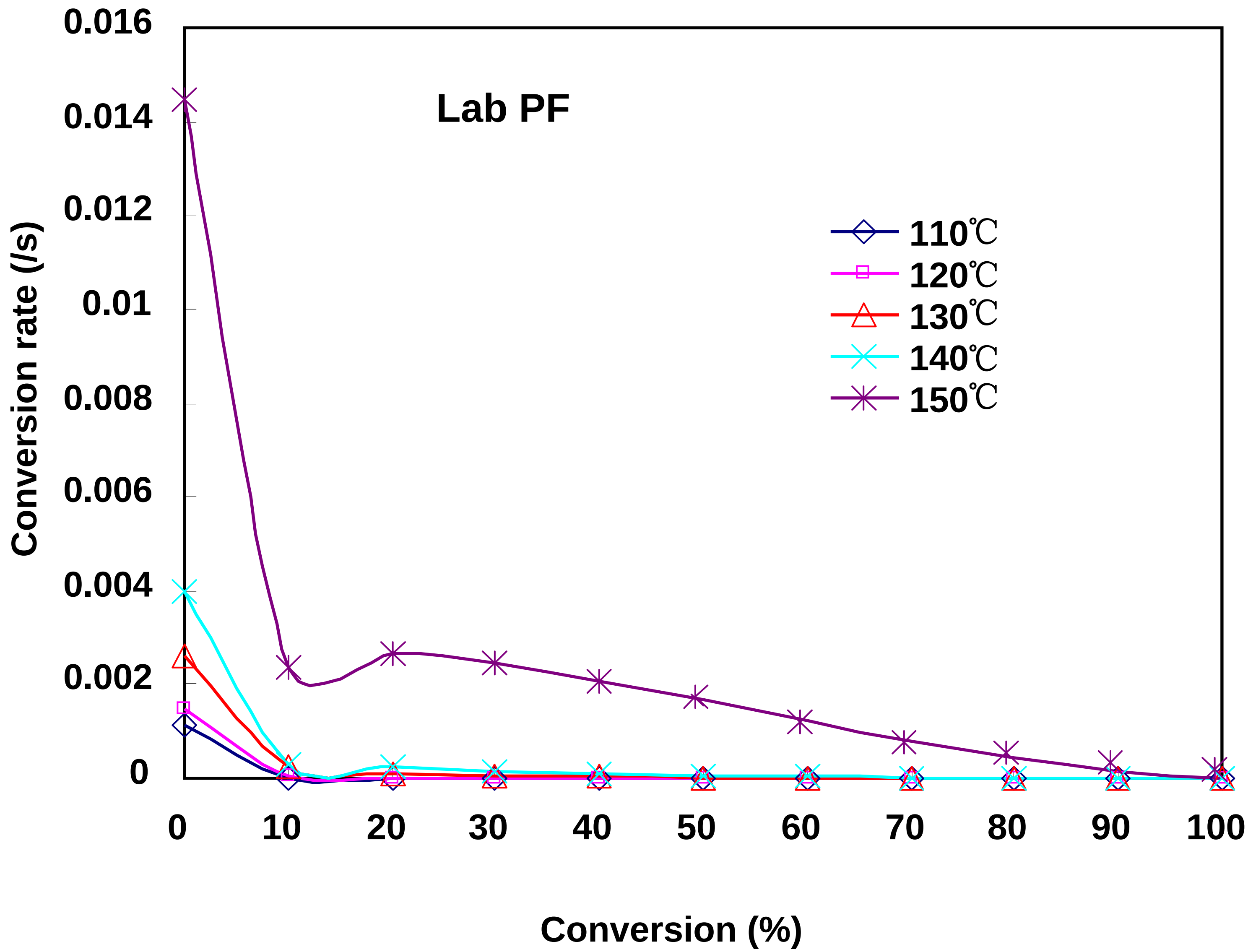
LBI PF: Liquefied mountain pine beetle infested pine bark PF resin;
LGP PF: Liquefied green pine bark PF resin

Bark-derived PF resin (Beetle infested)

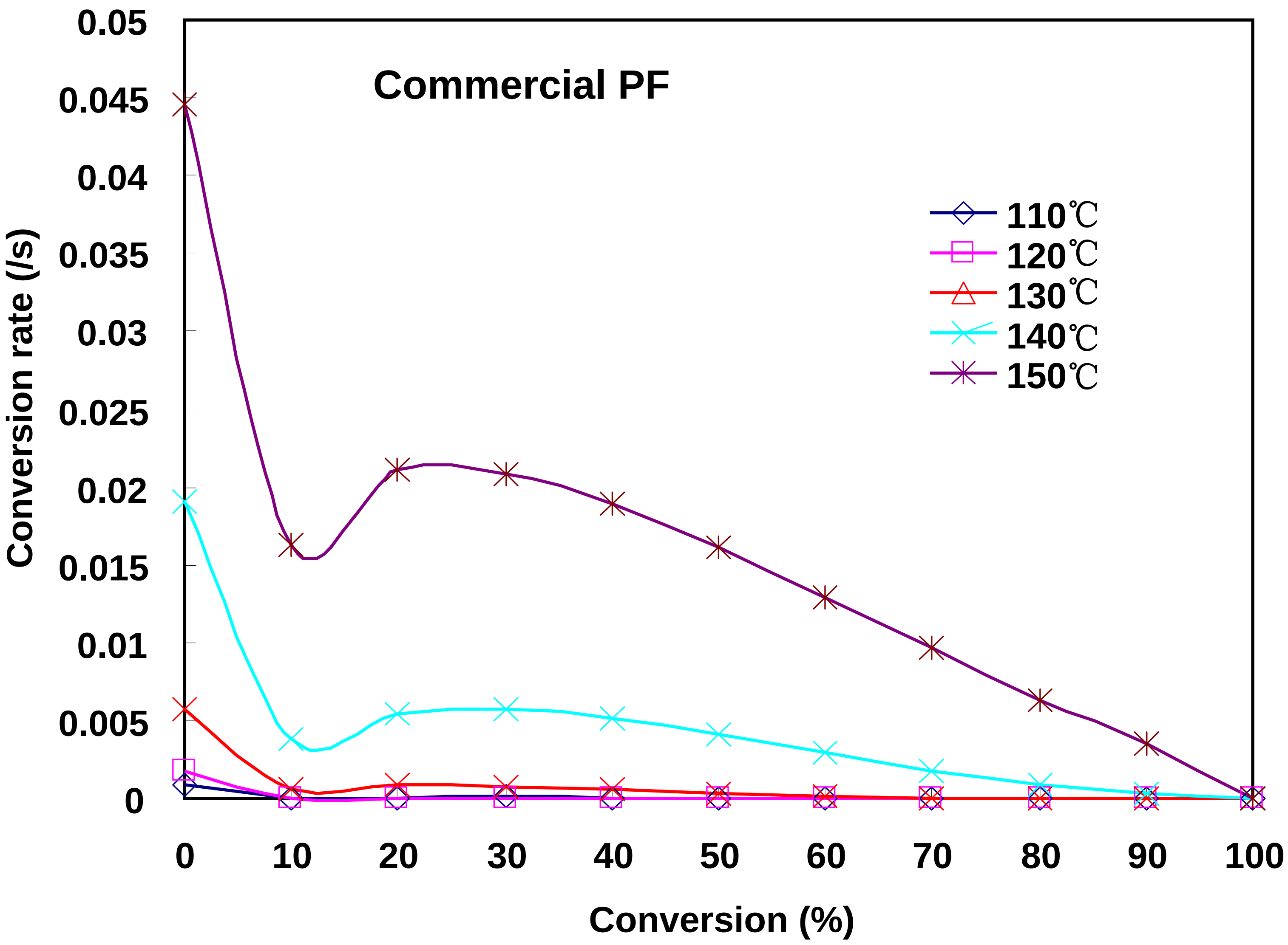



Bark-derived PF resin (Non infested)
LGP PF
110℃
120℃
130℃
140℃
150℃
Conversion rate (/s)
0.02
0.015
0.01
0.005
0
0
10
20
30
40
50
60
70
80
90
100
Conversion (%)

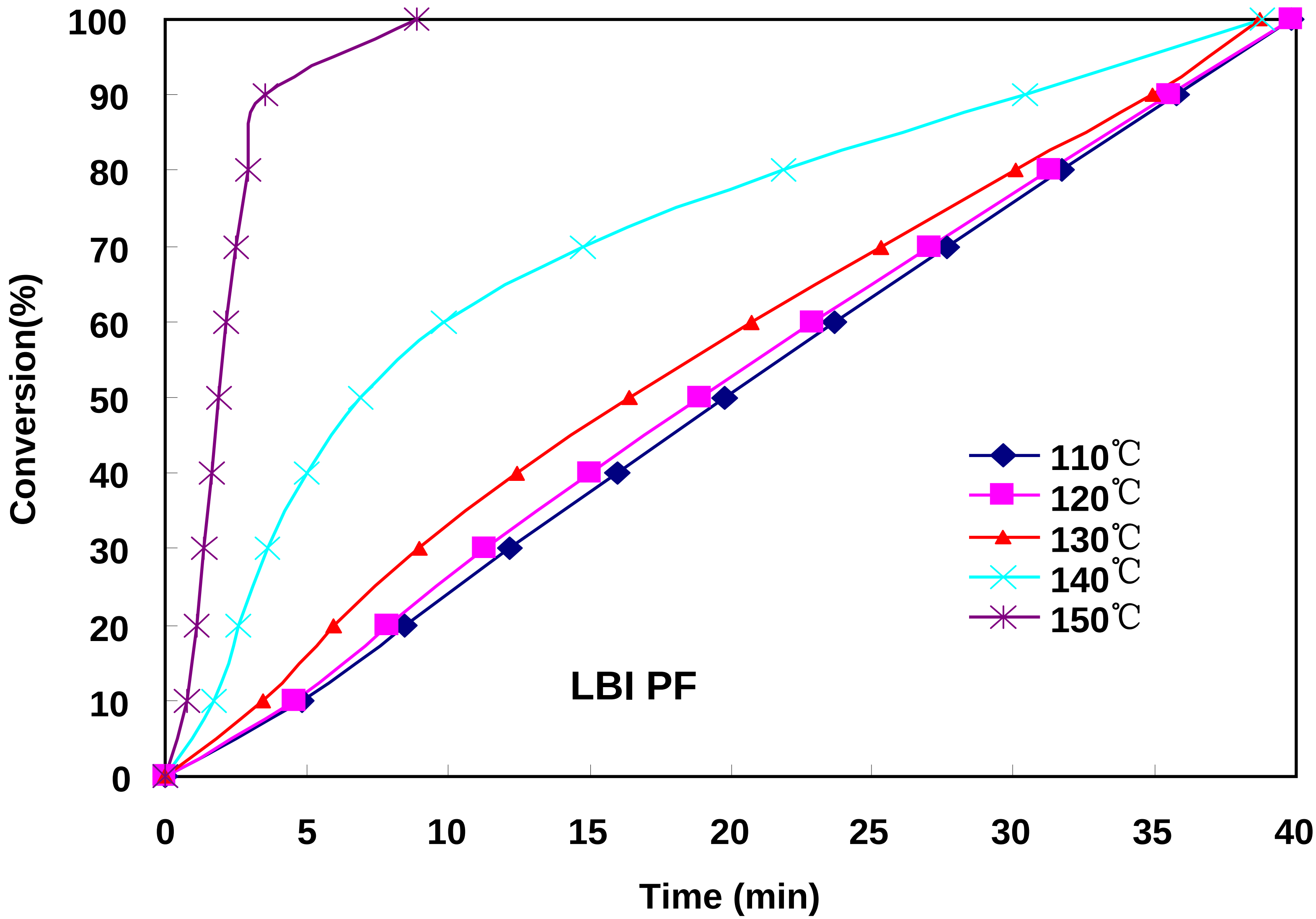
Lab made PF resin



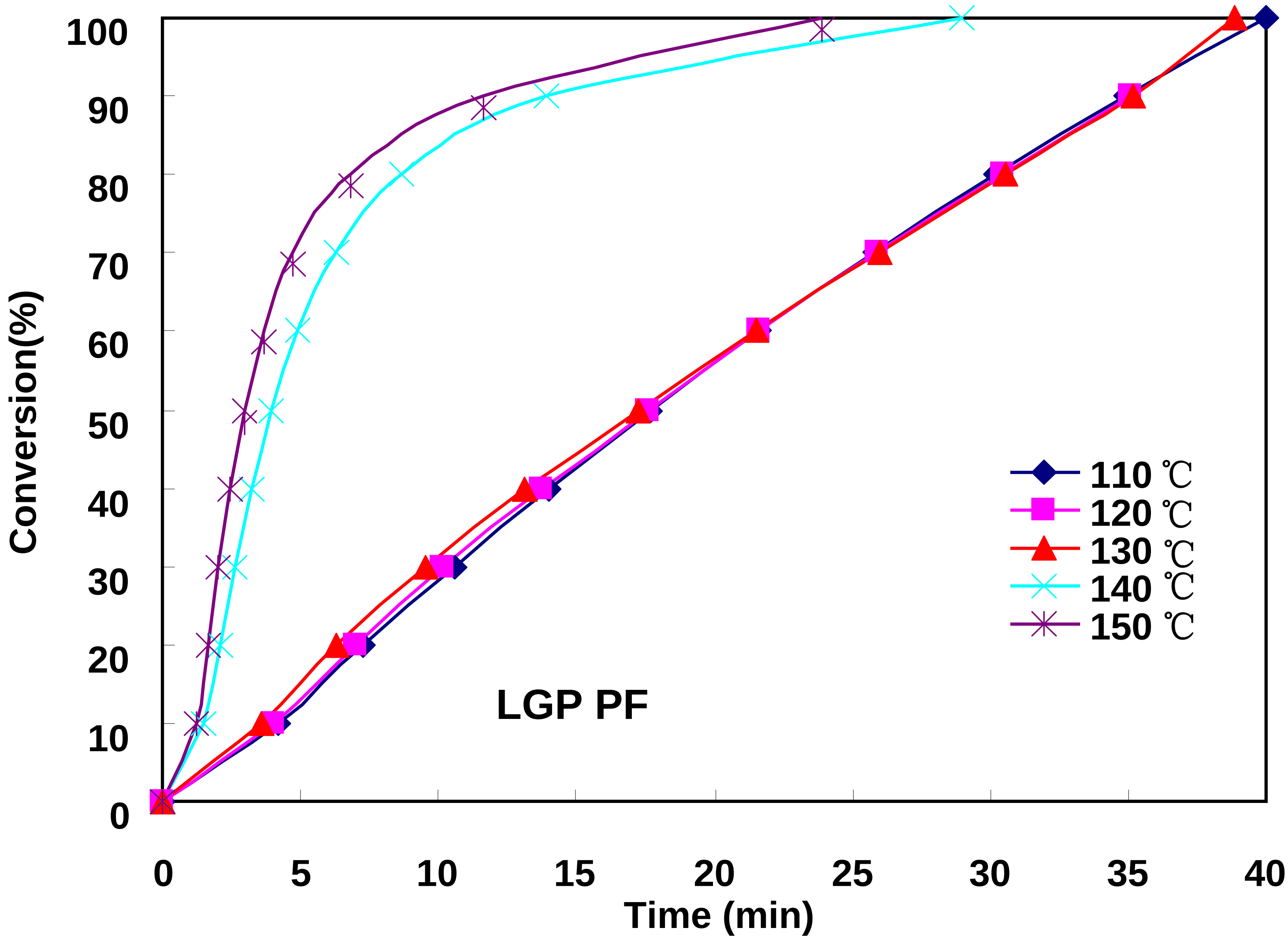
Commercial PF resin



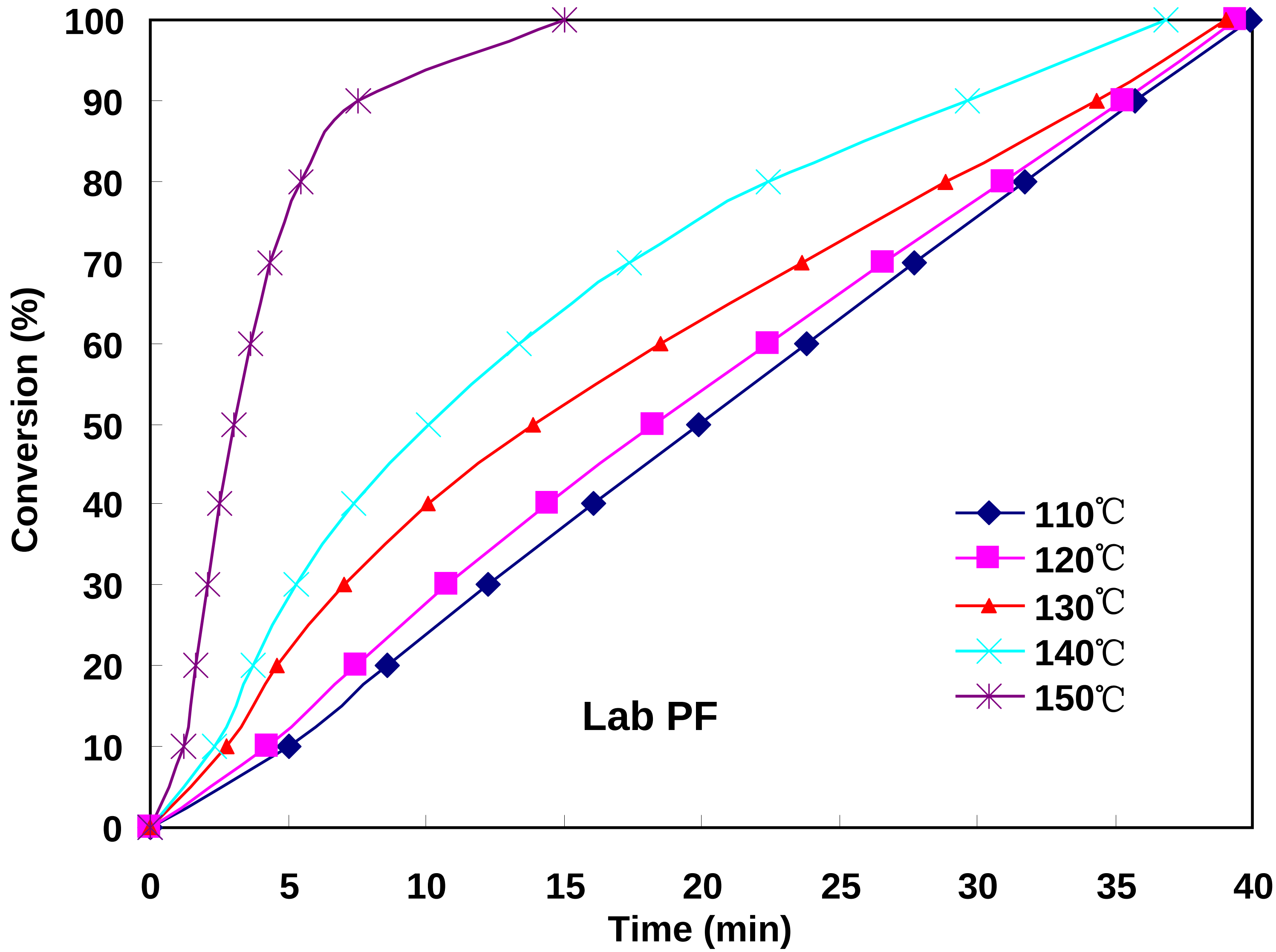
Bark-derived PF resin (Beetle infested)

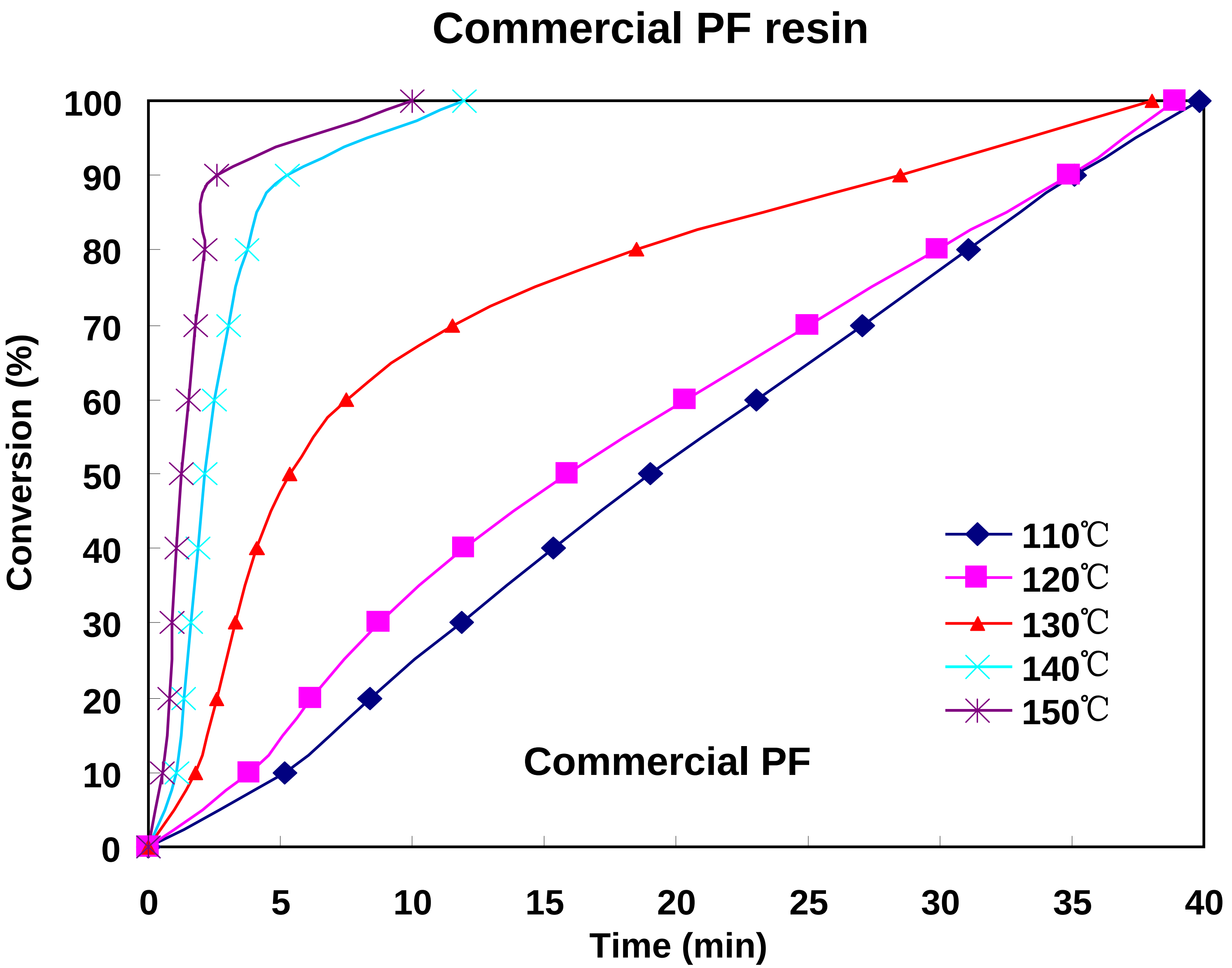


Bark-derived PF resin (Non infested)

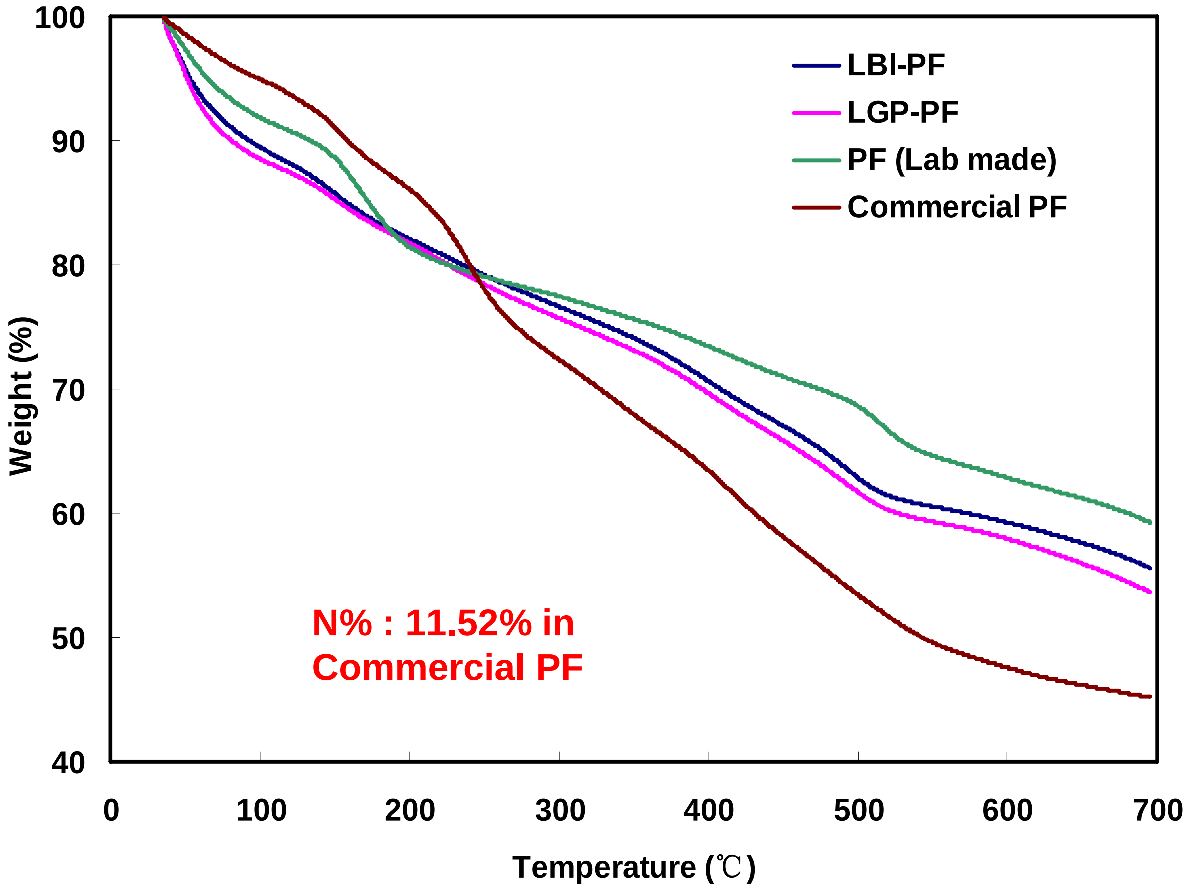


Lab made PF resin



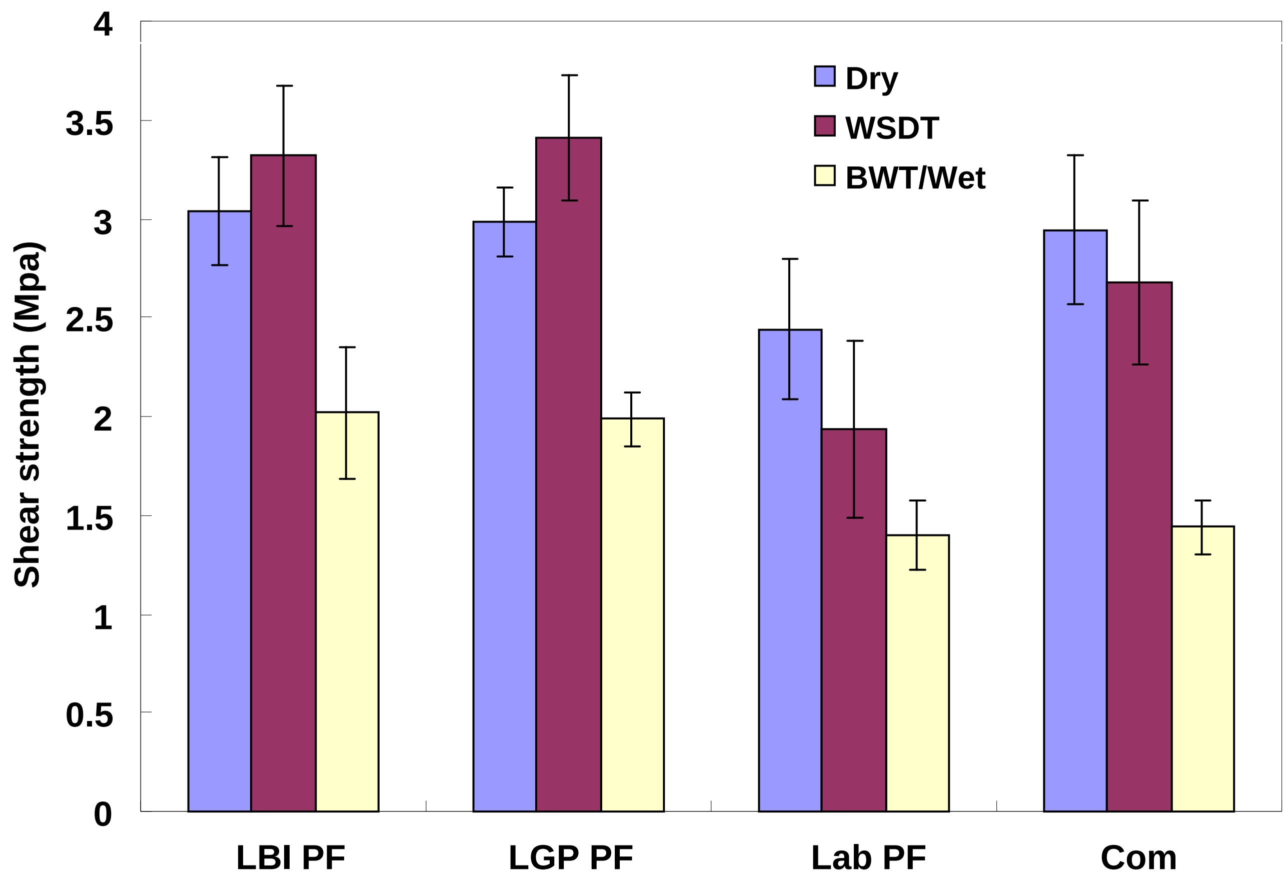

Commercial PF resin
Conversion (%)
Time (min)
0
10
20
30
40
50
60
70
80
90
100
0
5
10
15
20
25
30
35
40
110℃
120℃
130℃
140℃
150℃
Commercial PF

Thermal Stability of Cured Resins



LBI PF: Liquefied mountain pine beetle infested pine bark PF resin;
LGP PF: Liquefied green pine bark PF resin

Shear strength of board prepared by different adhesives



WSAD: specimens were soaked in water at room temperature for 24h, and then dried for 24h at room temperature, then for test.

BWT/Wet: specimens were boiled in water for 4h, dried for 20h at 63℃±2 ℃ ,boiled in water again for 4h, then cooled down with tap water and for test.

Conclusions

- **Bark-derived PF resins have larger Mw, PI and shorter gel time.**
- **All the resins exhibit both n-th order and autocatalytic cure mechanism.**
- **The post curing thermal stability of the BPF resins was similar to Lab PF but differed significantly from commercial PF resins.**
- **BPF resins showed highest wet bonding strengths.**
- **Beetle infestation was shown to have no negative effect on the bonding properties of the BPF resins.**
- **Bark from the mountain pine beetle infested lodgepole pine is a suitable material to partly replace phenol to synthesize phenolic resins.**

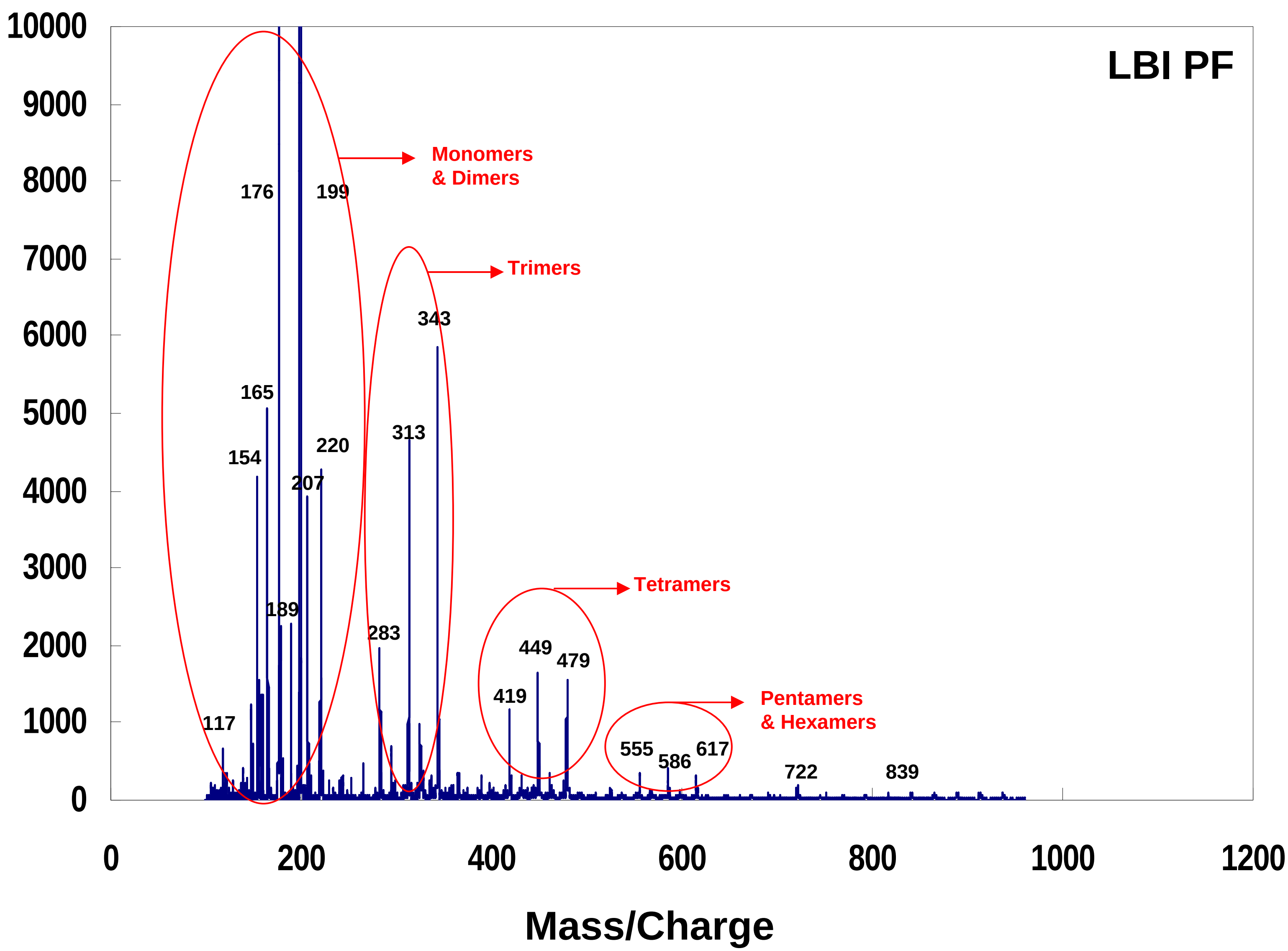
Acknowledgement

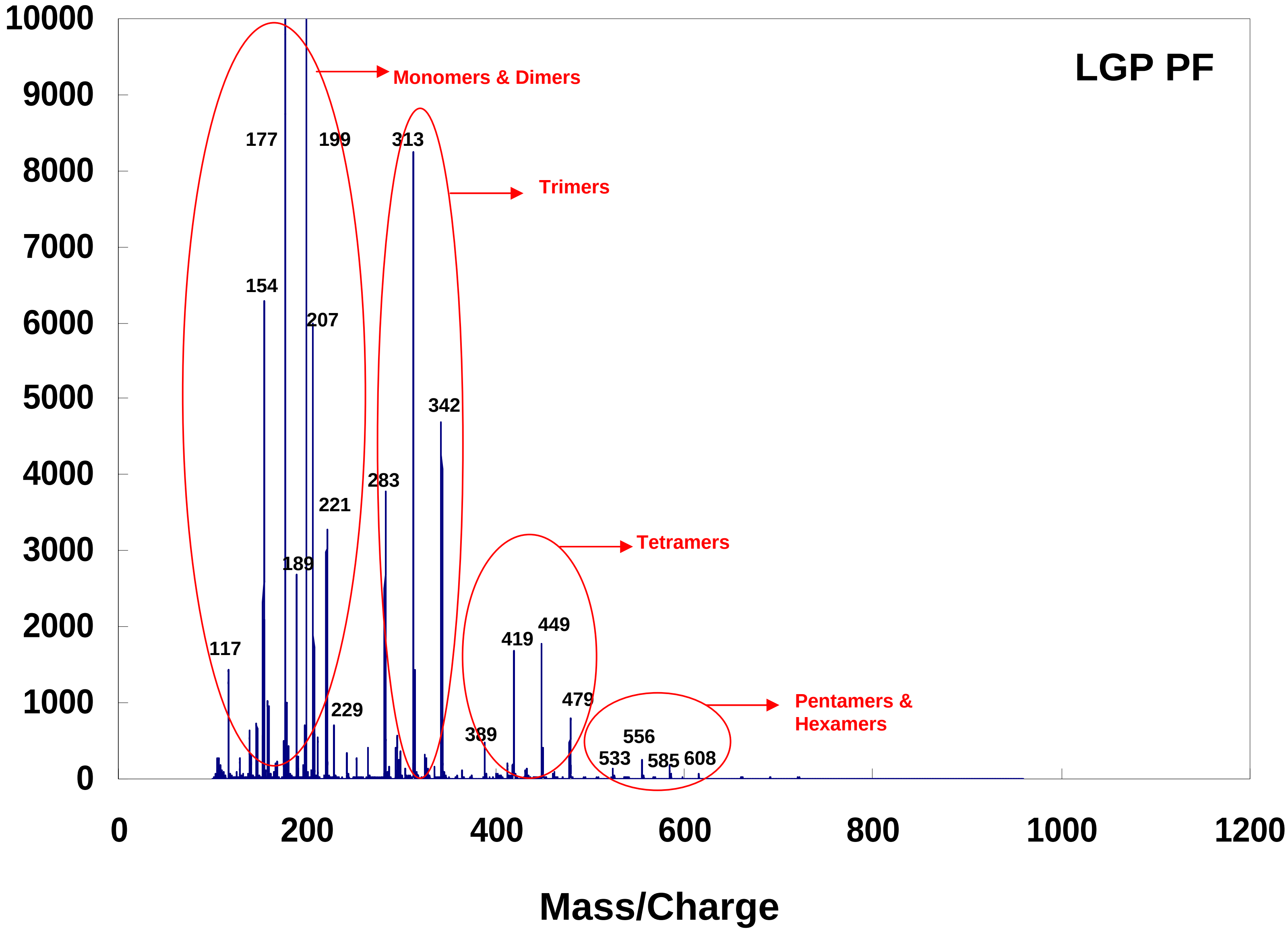
- Prof. Ning Yan & Martin Feng.
- FP Innovation Forintek Division
- Gireesh Gupta and Tony Ung for lap-shear test
- Syed Abthagir Pitchai Mydeen for kindly help.
- Lab-mates for suggestions and discussions.

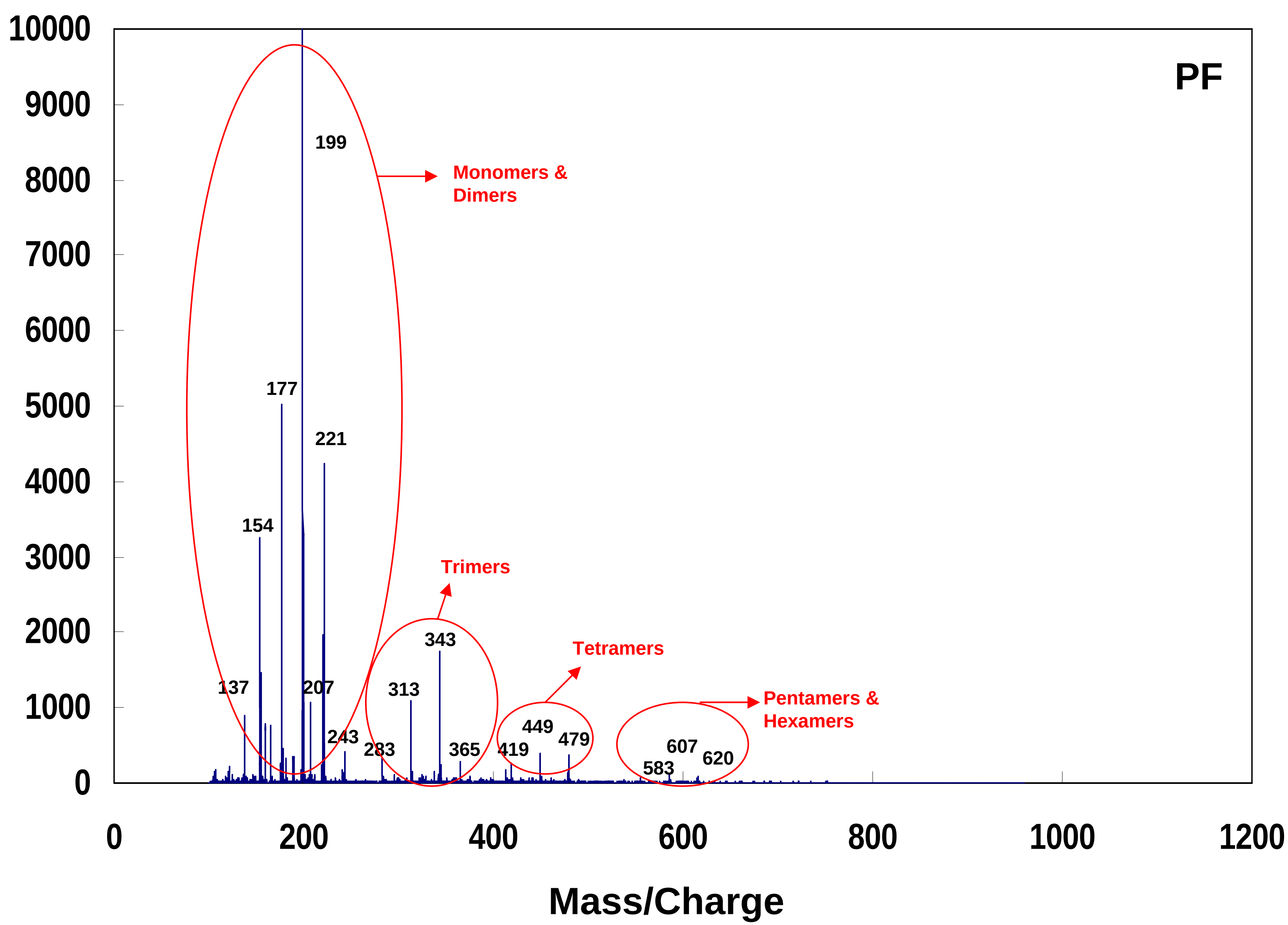
Thanks!

Any Questions?

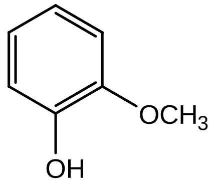
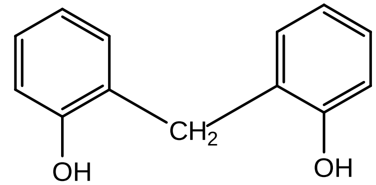
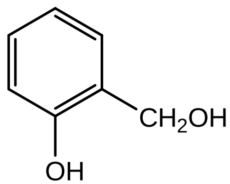
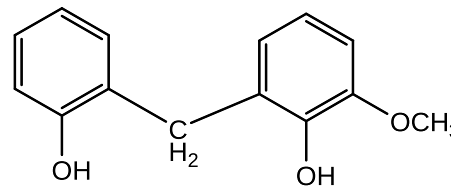
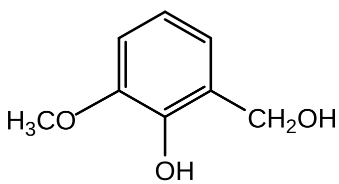
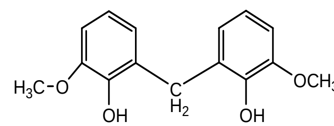
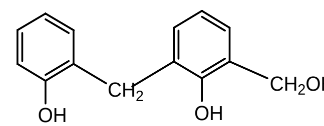
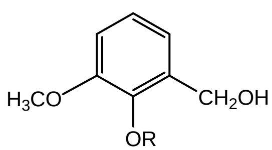
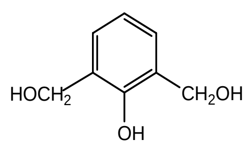
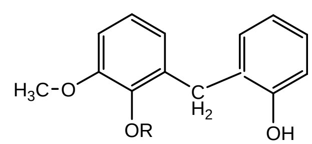
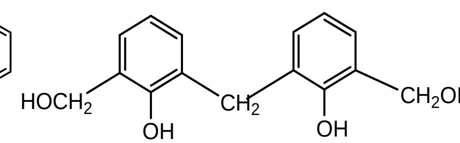
Backup slides


LBI PF
Monomers
& Dimers
Trimers
Tetramers
Pentamers
& Hexamers
176
199
165
154
220
207
189
117
343
313
283
449
479
419
555
586
617
722
839
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0
200
400
600
800
1000
1200
Mass/Charge


LGP PF
Monomers & Dimers
Trimers
Tetramers
Pentamers &
Hexamers
177
199
313
154
207
342
283
221
189
117
229
419
449
479
389
556
533
585
608
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0
200
400
600
800
1000
1200
Mass/Charge



PF
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0
200
400
600
800
1000
1200
Mass/Charge
199
177
221
154
137
207
243
283
313
343
365
419
449
479
583
607
620
Monomers & Dimers
Trimers
Tetramers
Pentamers & Hexamers

Mass	Possible Structures	Mass	Possible Structures
117		**199**	
137		**207**	
154		**221, 229**	 
165, 177	 	**243**	 
	Monomers		**Dimers**