Adhesive Technologies Satisfying Stringent Formaldehyde Limits

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Malaysia

Chimar Hellas S.A.

CHIMAR activities

- ✓ Developer and supplier of technology for the industrial production and APPLICATION of Formaldehyde-based resins and additives in the production of composite wood panels.

  Focus on safe, environmentally friendly technologies.

- ✓ Engineering services for formaldehyde and resin plants

- ✓ Versatility of services: R&D for third parties, Technical support for resin, WBP producers & OEMs, Specialty chemicals production upon request (Hardeners, FR, Wetting agents), Accredited formaldehyde testing, Resin and panel analysis, IPR protection, Quality Management Systems, Industrial Equipment representation

- ✓ Acting globally and helping locally

Re-classification of Formaldehyde (1/2)

•**World Health Organisation's International Agency for Cancer Research (IARC)** recommended (monograph vol. 88, 12/2006) classification of formaldehyde from Group 2A -"probably carcinogenic to humans" to **Group 1** - "carcinogenic to humans". This recommendation is not legally binding and was reaffirmed by IARC in October 2009.

•**EU** current formaldehyde classification: **category 2-suspected human carcinogen.** New classification of the European Chemicals Agency (ECHA) category **1B-presumed human carcinogen** will become effective EU-law as of 01.04.2015

•**US** EPA current classification: **probable human carcinogen (B1).** Draft toxicological review of formaldehyde-inhalation assessment released June 2010 supports carcinogenic effects.

Re-classification of Formaldehyde (2/2)

- Numerous toxicological & cancer studies for formaldehyde since 1980. Major studies in Europe and USA, some still ongoing.

- **CARB** formaldehyde emission limits for composite wood products are in force throughout the US as from **January 2013**.

- Variation among national Occupational Exposure Limits (OEL) for formaldehyde around the world. The lowest OEL levels are established in Europe and range from 0.3 to 0.5 ppm.

European Formaldehyde classes

- **E1** with limit value based on EN 717-1 (chamber method) of 0.1ppm as per harmonized standard EN13986 (wood-based panels)

- New proposed **E1 plus** with limit value based on EN 717-1 (chamber method) of 0.065ppm (wood-based panels)

US CARB Formaldehyde standards

- Phase 2 standards are now in effect for all products included in the California Air Resources Board (CARB) Airborne Toxic Control Measure to Reduce Formaldehyde Emissions From Composite Wood Products

	CARB Phase 2 Emissions Standards				
	Emissions Standards (ppm)	ULEF – Reduced		NAF & ULEF – Exempt	
		Cap (ppm)	Target (90% of Samples – ppm)	Cap (ppm)	Target (90% of Samples – ppm)
Particleboard	0.09	0.08	≤ 0.05	0.06	≤ 0.04
Thin MDF	0.13	0.11	≤0.08		
MDF	0.11	0.09	≤0.06		
HWPW-VC	0.05	0.05		0.05	
HWPW-CC	0.05				

Ashlee Cribb, GP, Wood Adhesives 2013

Japanese Formaldehyde standards

Board class	HCHO limit	Test method
F****/SE0	≤ 0.3mg/L	JIS A 1460
F***/E0	≤ 0.5mg/L	JIS A 1460
F**	≤ 1.5mg/L	JIS A 1460

F** class in Japan is more or less equivalent to European E1-class
F*** and F**** are of much lower emission than the E1
F**** emission is close to the emission of solid untreated wood

Solutions for Formaldehyde emission reduction

- **Innovative systems** of adhesive resins and chemical additives, the synergistic action between them providing successful gluing performance and desirable emission properties
- **Advanced technologies for adhesive resin synthesis,** enabling optimum use of production conditions to obtain resins with target gluing and emission performance
- **Bio-derived adhesives based on natural products and materials** (e.g. lignin, tannin, starch) combining the utilisation of renewable raw materials with high bonding performance and reduced formaldehyde emission at the same time.

Data from “E0” PB, 16mm (1/2)

E0 PB, UMF + FS	
Press Factor, s/mm	4.2
Resin Factor, % core/surface	8 / 10
Scavenger level, % s/s on resin	10
Board Density, kg/m^3	630
IB, N/mm^2	0.42 – 0.45
MOR, N/mm^2	13-15
Formaldehyde content, EN 120, mg/100g	2.5 – 3.0
Cost Vs E1, €/m^3	**+3**

Data from “E0” PB, 16mm (2/2)

E0 PB, UMF	
Press Factor, s/mm	4.8
Resin Factor, % core/surface	9 / 9
Scavenger level, % s/s on resin	-
Board Density, kg/m^3	650
IB, N/mm^2	0.45 – 0.48
MOR, N/mm^2	14-16
Formaldehyde content, EN 120, mg/100g	2.5 – 3.0
Cost Vs E1, €/m^3	**+3**

Data from “E0” thin HDF, 3mm

E0 HDF, UMF	
Press Factor, s/mm	6.5
Resin Factor, % core/surface	13
Scavenger level, % s/s on resin	15
Board Density, kg/m^3	880
IB, N/mm^2	0.8 – 1.2
MOR, N/mm^2	35 – 40
Formaldehyde content, EN 120, mg/100g	3.0 – 3.5
Cost Vs E1, €/m^3	**+6**

R&D on Bio-based Resins

- Phenol-Formaldehyde resins with partial substitution of phenol by natural materials
- Urea-formaldehyde resins with natural products as additives
- Totally natural resins
- Achievements at the laboratory, pilot and industrial scale

Global Technology Provider: Resin & Wood Panel Industries

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Natural raw materials		Production scale			Type of wood panel
		Industrial	Pilot	Lab	
		Phenol substitution level, %			
1	Liquefied Olive stone	50		75	Plywood
2	Wood pyrolysis liquid (Bio-oil)	20			Plywood
		40	50		OSB
3	Torrefaction Condensates			40	Plywood
4	Lignin	50	50	80	Plywood
5	Tannin, quebracho	30			Plywood
6	Tannin, pine	~50% resin replacement			PB
7	Tannin, mix			Totally natural binder	PB
8	Soy Protein			25	Plywood
9	CNSL			10	Plywood/PB

Partial Phenol replacement in PF resins

Potential for Industrial Application:

- Technical studies showed that 50% replacement of phenol by Lignin is possible on an industrial scale
- Due to availability and price, Lignin is the most prominent phenol substitute
- Technology and Lignin supply readily available world-wide

Applying natural materials for biolatex® polymers

Biopolymer Source + Chemicals

Proprietary Continuous Manufacturing Process

Biolatex® Dry Polymer

Patented Formula

Patented Process

Patented Product

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Independent Lab Evaluation: Biobased Binders

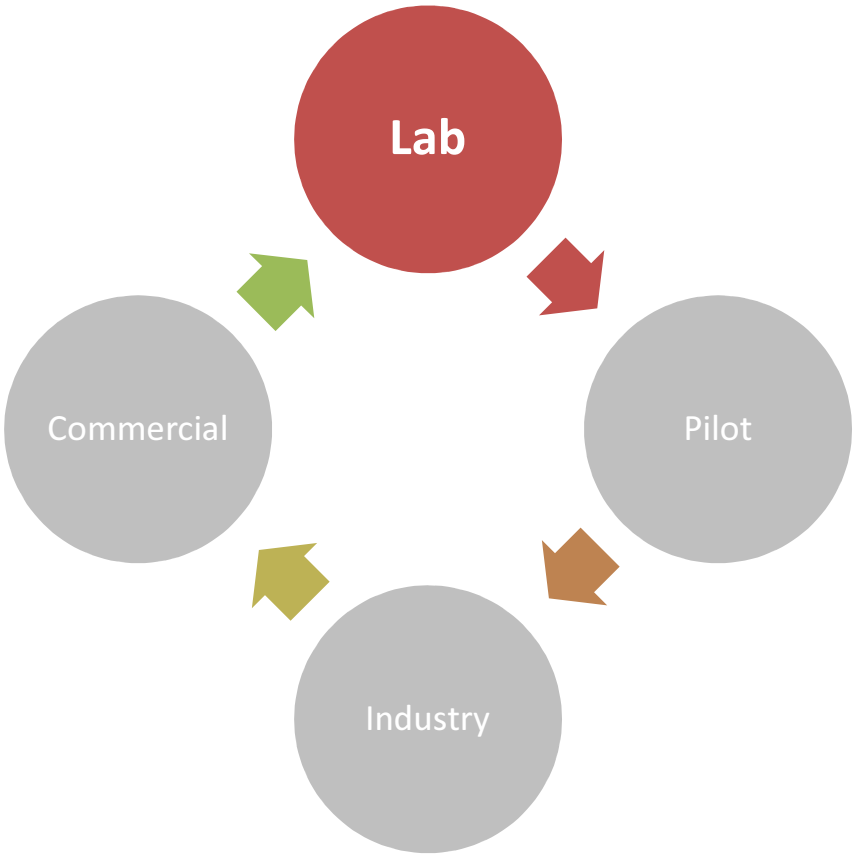
ECOSYNTHETIX®

SUSTAINABLE POLYMERS FOR PLANET EARTH®

Lab, pilot and industry trials

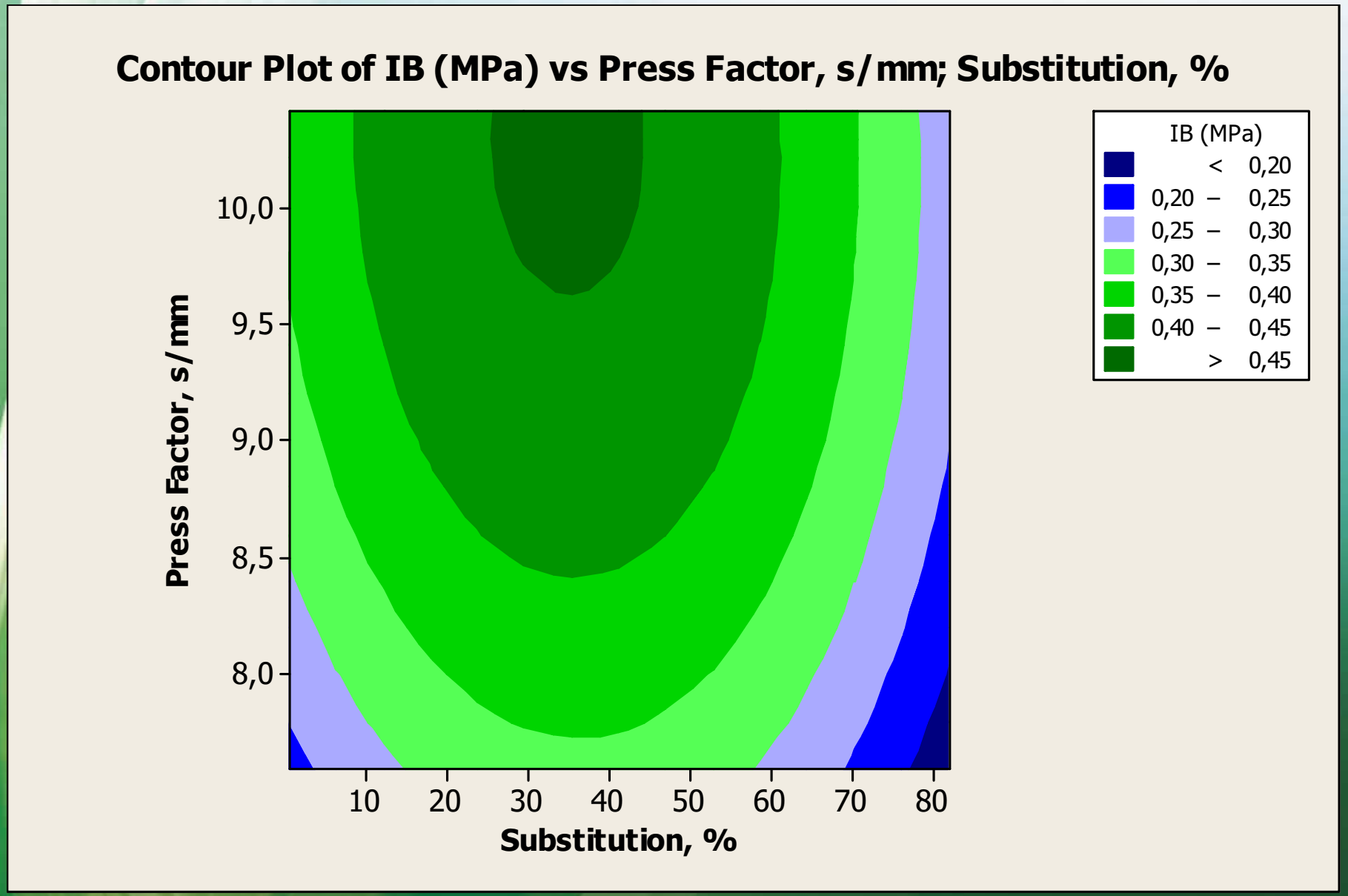
Lab Facility:

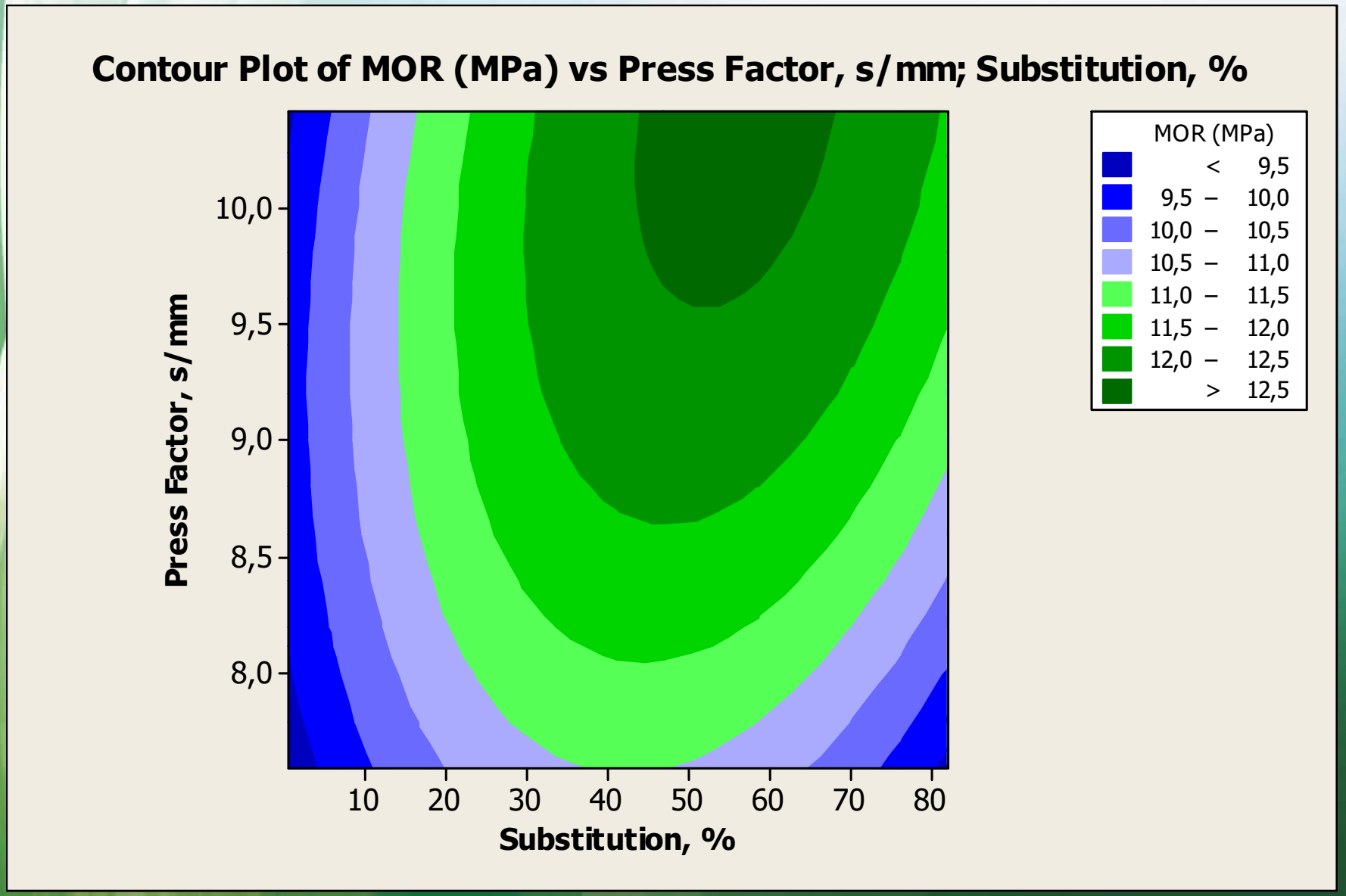
Chimar Laboratories
Accredited Test Lab
Thessaloniki, Greece

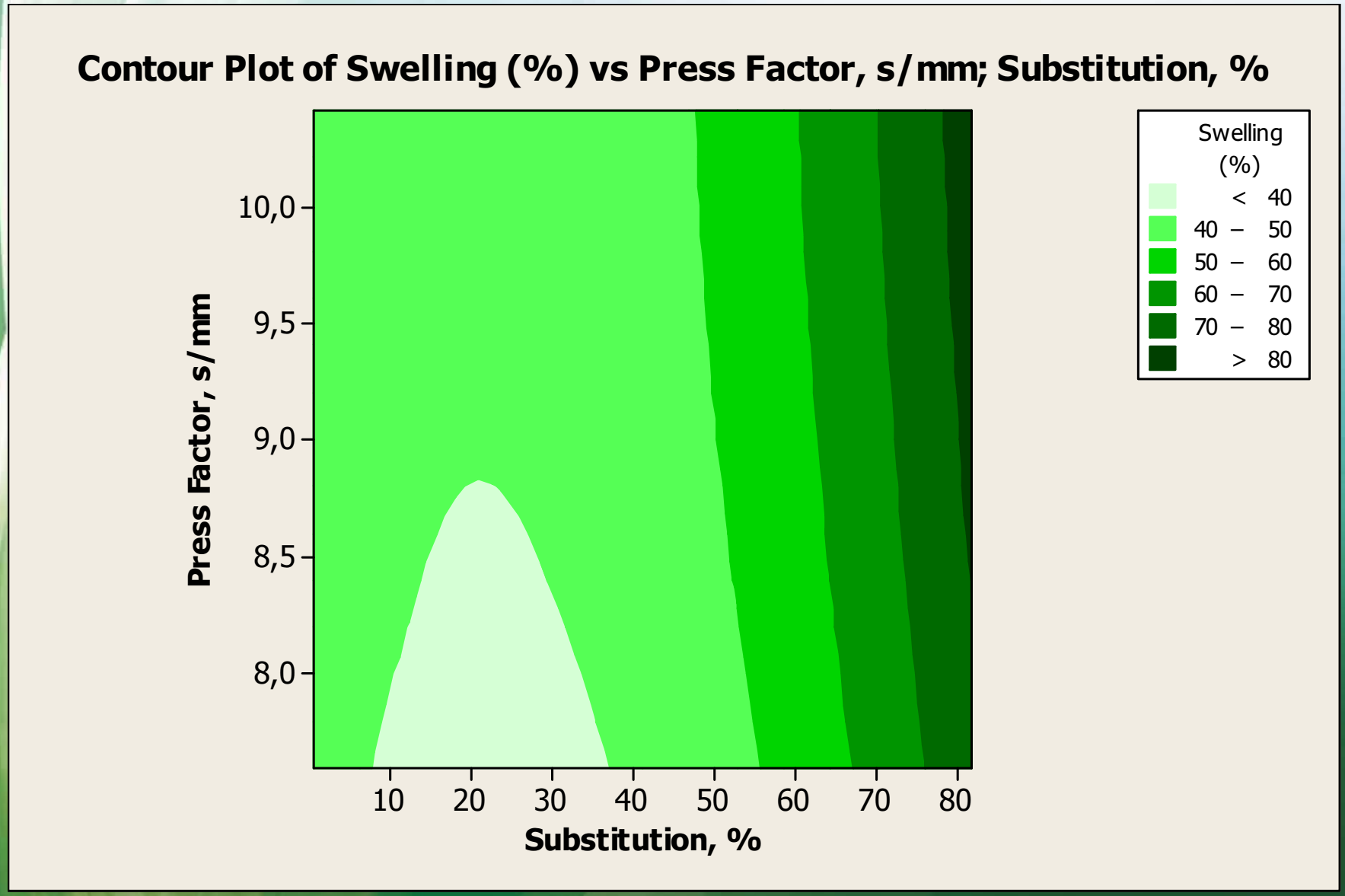


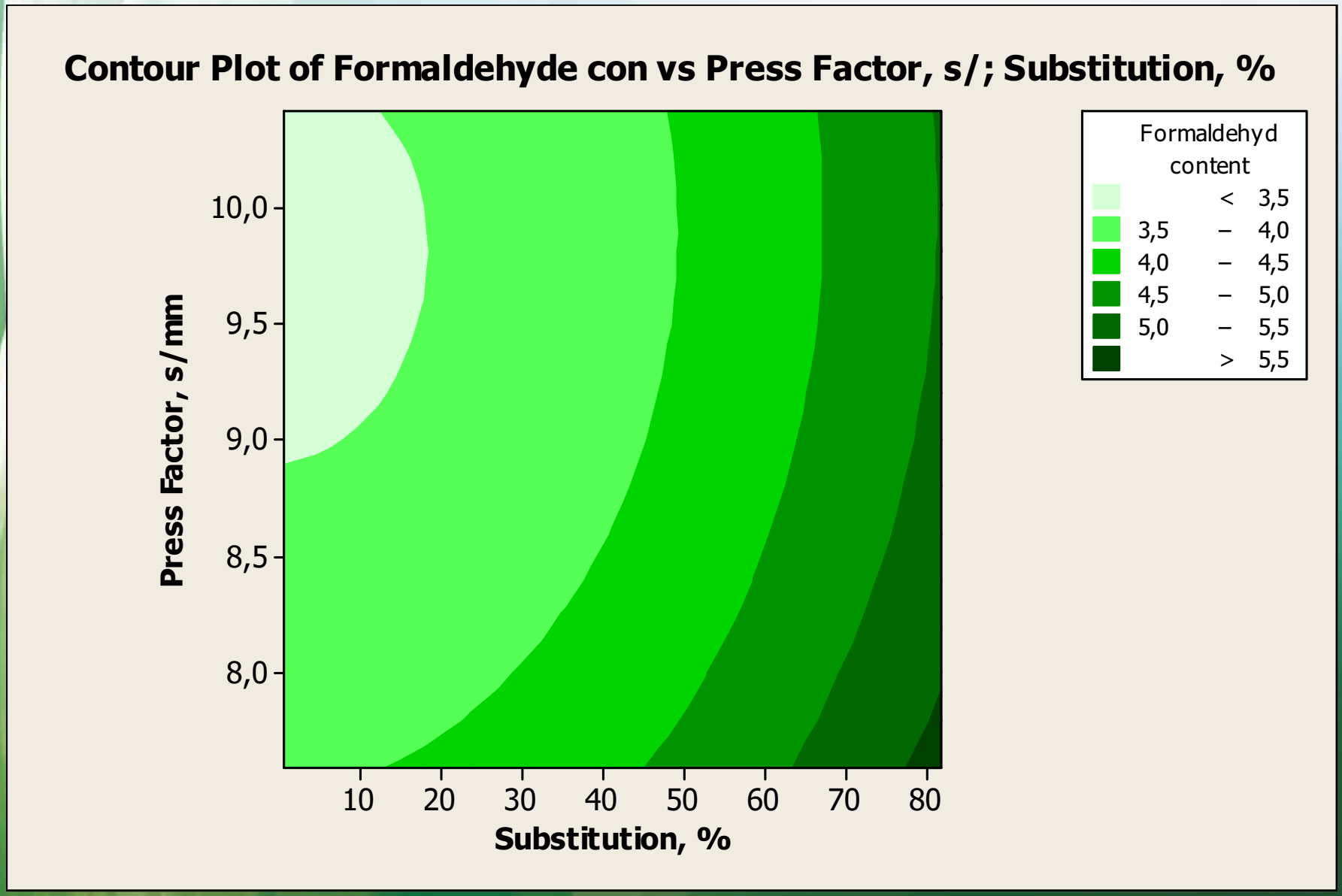
Lab evaluation settings

Panel product	Single layer particleboard
Panel size, mm x mm x mm	440 x 440 x 16
Panel density, kg/m^3	660
Initial resin loading, %on dry wood	8
Paraffin wax loading, %on dry wood	0.5
Hardener loading $(NH_4)_2SO_4$, %	3
Mat moisture, %	11.5
Resin type	UmF 096/066RS
Press temperature, ^oC	210
Wood mix: Scots pine, maritime pine & european black pine	


Contour Plot of IB (MPa) vs Press Factor, s/mm; Substitution, %
IB (MPa)
< 0,20
0,20 – 0,25
0,25 – 0,30
0,30 – 0,35
0,35 – 0,40
0,40 – 0,45
> 0,45
Press Factor, s/mm
10,0
9,5
9,0
8,5
8,0
10
20
30
40
50
60
70
80
Substitution, %

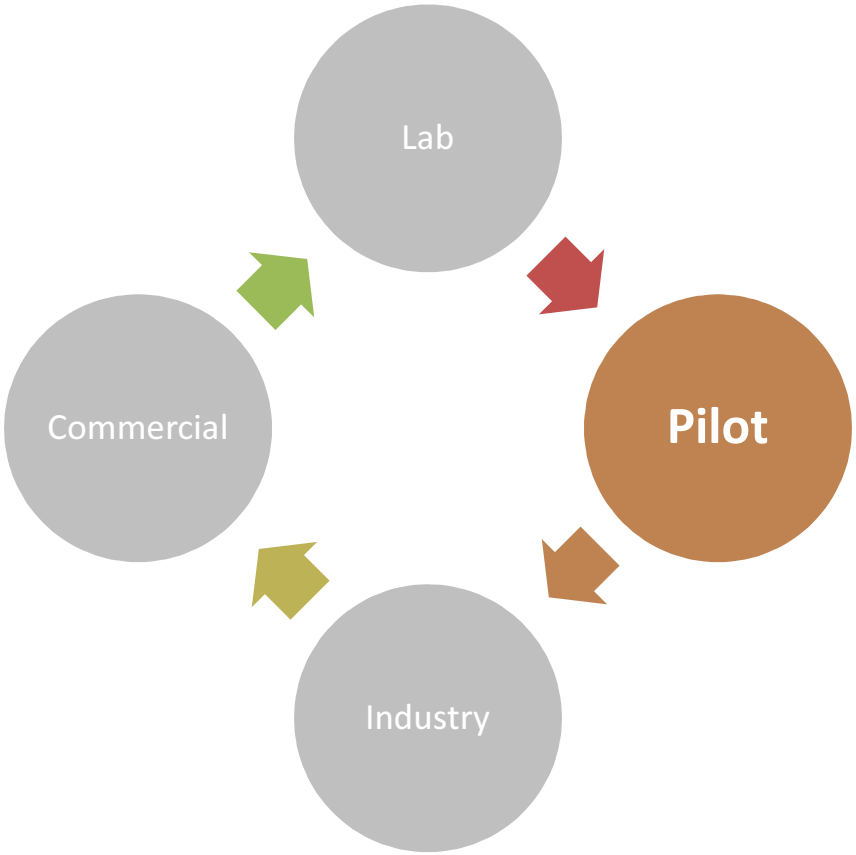

Contour Plot of MOR (MPa) vs Press Factor, s/mm; Substitution, %
Press Factor, s/mm
10,0
9,5
9,0
8,5
8,0
10
20
30
40
50
60
70
80
Substitution, %
MOR (MPa)
< 9,5
9,5 – 10,0
10,0 – 10,5
10,5 – 11,0
11,0 – 11,5
11,5 – 12,0
12,0 – 12,5
> 12,5


Contour Plot of Swelling (%) vs Press Factor, s/mm; Substitution, %
Press Factor, s/mm
10,0
9,5
9,0
8,5
8,0
10
20
30
40
50
60
70
80
Substitution, %
Swelling (%)
< 40
40 – 50
50 – 60
60 – 70
70 – 80
> 80



Formaldehyde content in mg/100g O.D.B. according to EN 120 (Perforator Method)

Lab, pilot and industry trials



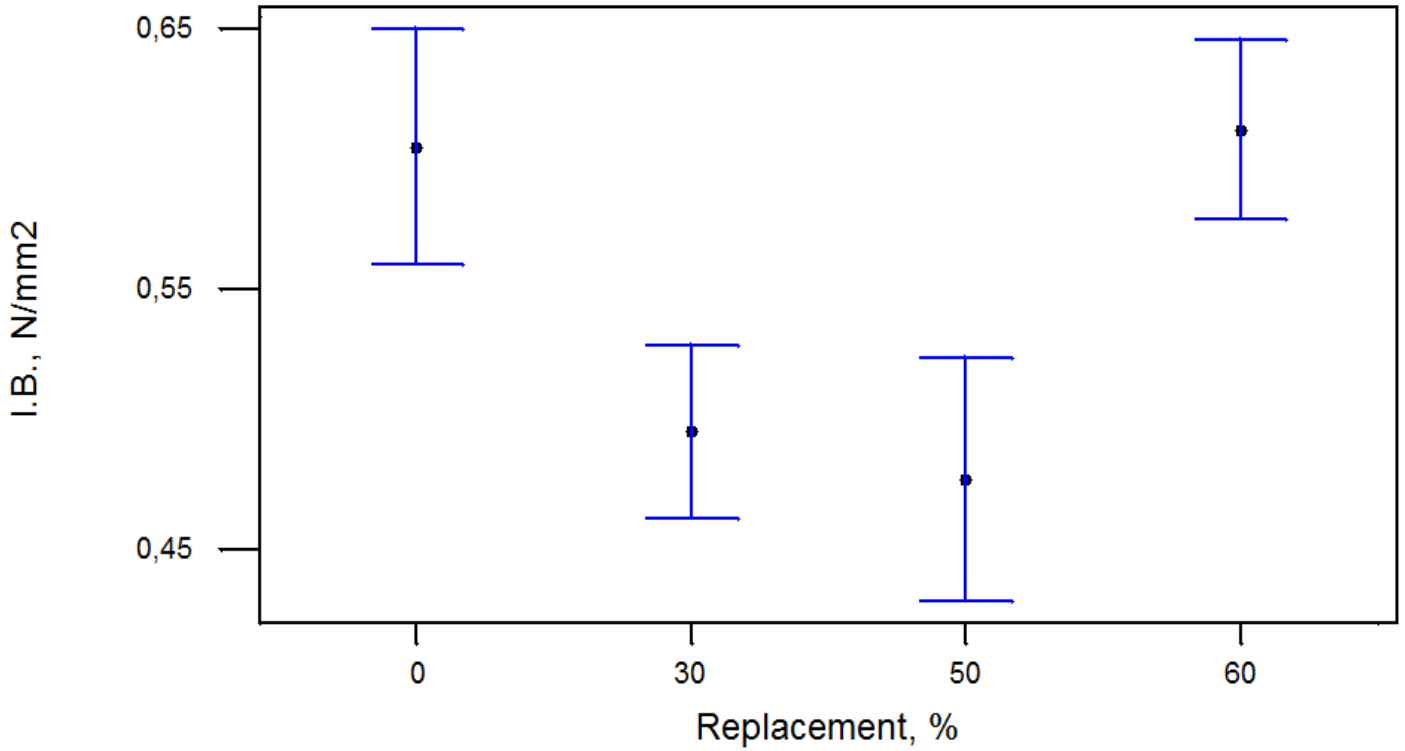
Pilot Trial:

Alberta Innovates Technology Futures = "AITF"
Edmonton, Alberta

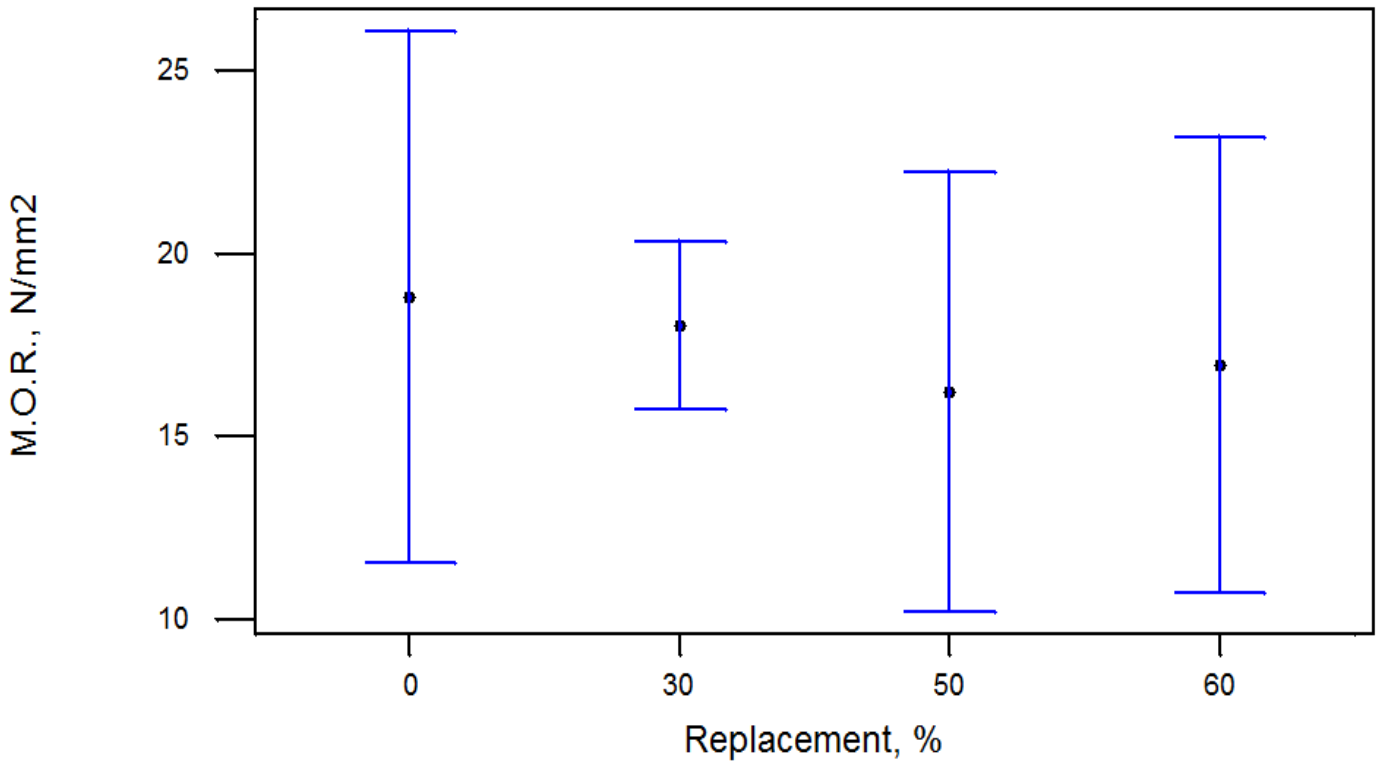
“AITF” production settings

Panel product	Single layer MDF
Panel size, mm x mm x mm	610 x 610 x 21.3
Panel density, kg/m^3	800
Initial resin loading, %on dry wood	12
Paraffin wax loading, %on dry wood	0.5
Hardener loading $(NH_4)_2SO_4$, %	0
Mat moisture, %	9 -11
Resin type	UF 096D
Press temperature, ^oC	160
Press cycle, s	600
Wood mix: 60% lodgepole pine, 40% white spruce with a small % of balsam fir	

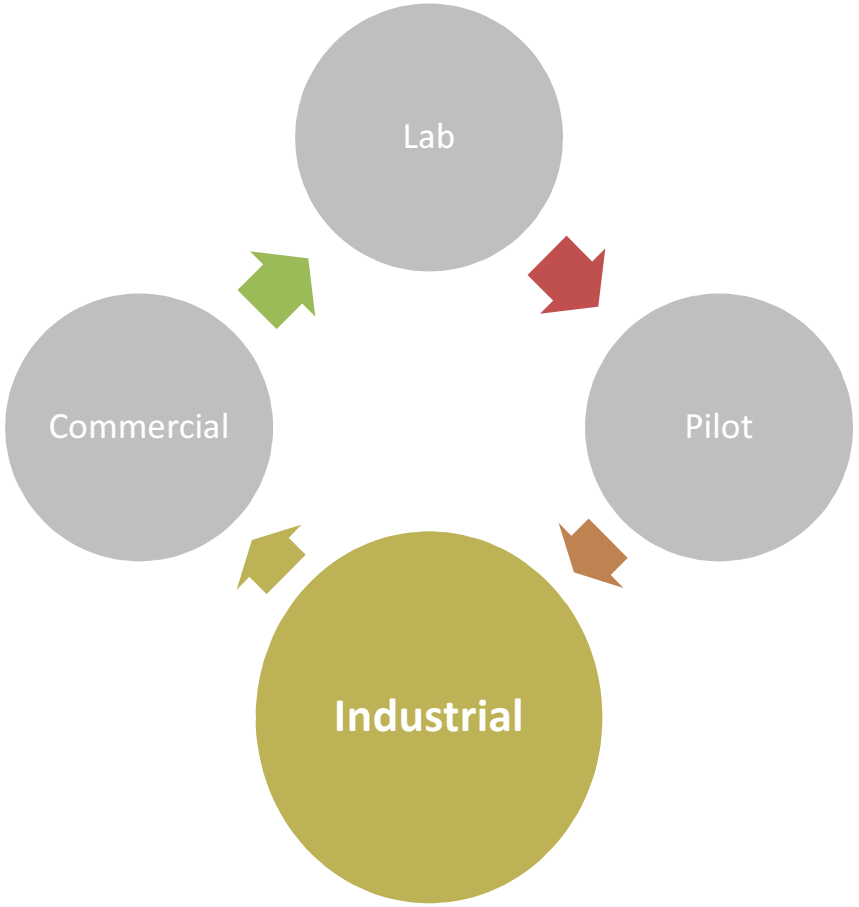
Pilot test at “AITF”
Internal bond versus replacement



Pilot Test at “AITF”
MOR versus replacement



Lab, pilot and industry trials



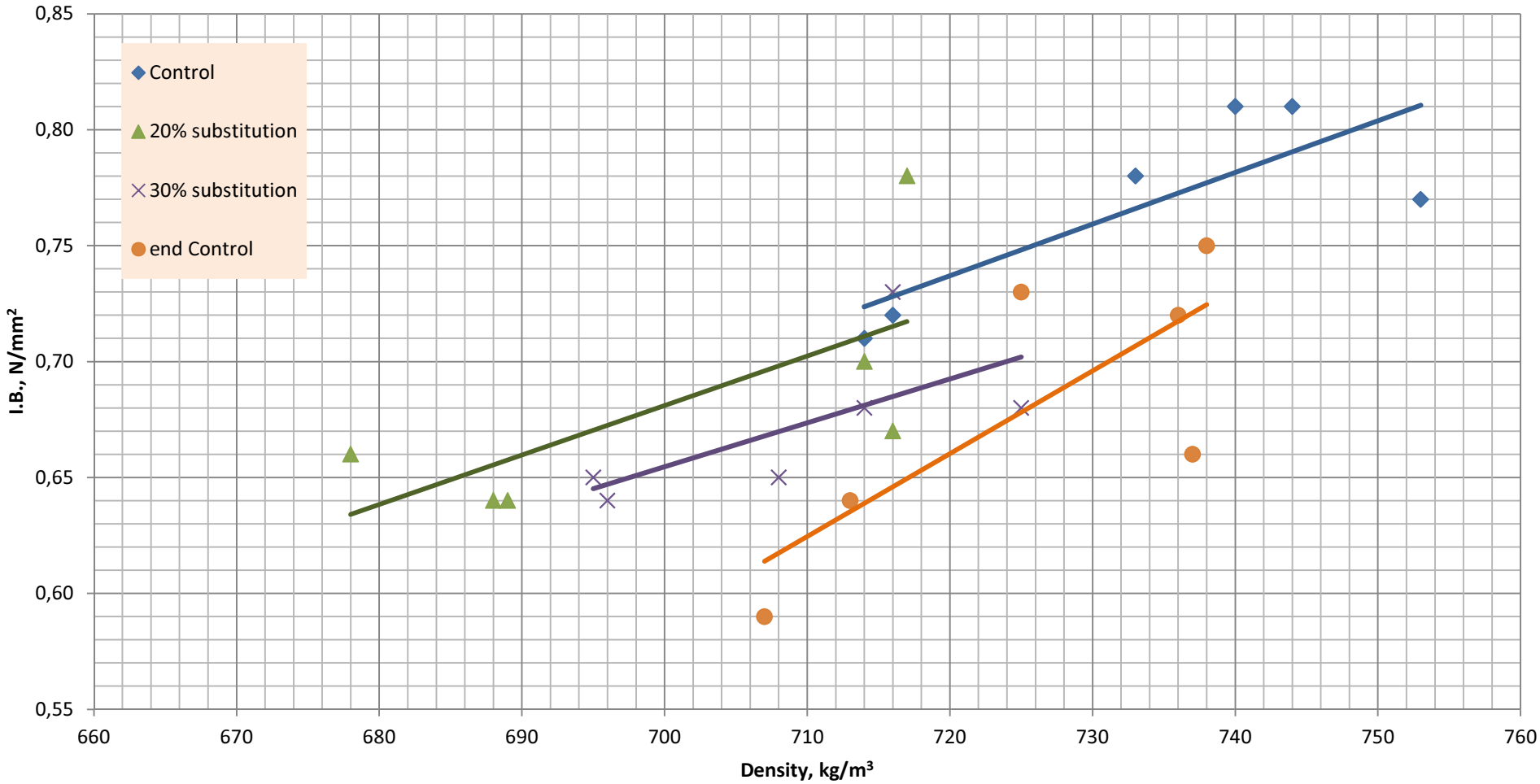
Industrial Trial:

MDF Production
European Region

Industrial MDF production settings

Panel product	Single layer MDF
Panel size, mm x mm x mm	610 x 610 x 19.5
Panel density, kg/m^3 (lb/ft^3)	700 – 720 (43.5 – 45.0)
Initial resin loading, %on dry wood	11
Paraffin wax loading, %on dry wood	0.5
Hardener loading $(NH_4)_2SO_4$, %	1.5
Mat moisture, %	9
Resin type	UF 096D
Press temperature, ^oC	240 – 220 – 210 –190
Press cycle, s	193.5
Wood mix: Scots pine (80%) and white poplar (20%)	

Industrial MDF Internal Bond (IB)



Industrial MDF results

	Control Start	Ex. #1	Ex. #2	Control End
% replacement	0	20	30	0
Density, kg/m^3	733	700	709	726
I.B., N/mm^2	0.77	0.68	0.67	0.68
M.O.R., N/mm^2		26.6	28.3	27.2
Moisture content, %		4.4	4.4	4.6
Formaldehyde emissions Gas analysis, (mg·m^{-2}·h^{-1})		4.2	4.1	3.3
Formaldehyde content at 6,5% MC mg/100g O.D.B.		7.9	8.7	7.4

0.69N/mm^2 is 100PSI
25.0N/mm^2 is 3,626PSI

Discussion

- The biolatex bio binders can substitute significant amounts of UF / UmF resin
- In lab, pilot and industrial scale
- Current applications:
  - MDF
  - Face PB
- Substitution ratio of two parts of UF / UmF by one part of biolatex supports economic viability
- More R&D is on the way to further improve performance to cost ratio and broaden application spectrum

CONCLUSIONS

The technologies and results presented show that the current stringent formaldehyde emission limits for composite panel products can be satisfied with the use of properly formulated adhesive systems at no sacrifice of the desirable panel properties and no need for significant modification of the operating conditions of the panel industry

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Thank you!