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Aqueous poly(lactic acid) copolymer dispersions as paperboard barrier coatings

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VTT

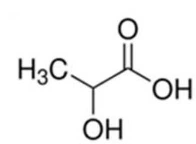
Aqueous (bio)polymer dispersions

- Polymer particles in nano- to micrometer size dispersed in water. During drying these particles coalescence into a uniform polymer layer.
- Highlights:
  - Enables thinner coatings than typically possible by extrusion,
  - Alternative application techniques (on- and off-machine, printing presses),
  - Freedom for preparing formulations with different additives.
- Lowlights:
  - Majority of current products are at least partly petroleum based,
  - Only few products provide all the required properties alone,
  - Recycling performance and viable end-of-life options to be clarified,
  - Positioning in EU directives/regulations for specific applications.

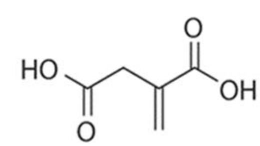
Cross-linkable poly(lactic acid) dispersions

- Typically PLA dispersions not feasible due to hydrolytic instability,
- Goal is to overcome this challenge:
  - Unsaturated cross-linkable copolymers prepared by bulk polycondensation,
  - Bio-based content of the polymer up to 100%,
  - Biodegradation in water is faster than with neat PLA,
  - Dispersions with the thermomechanical method with PVOH as a stabilizer,
  - Pilot coated dispersion has outperformed extruded PLA coatings.
- Applications include also self-healing materials for surface treatment and encapsulation of hydrophobic active compounds

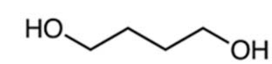
https://aaltodoc.aalto.fi/handle/123456789/23472
Mehtiö, T., J. App. Pol. Sci., vol. 134, issue 1, p. 44326 (1-8).
Rämö, V. Eur. Pol. J., vol. 48, issue 8, p. 1495–1503.



D,L – lactic acid



Itaconic acid

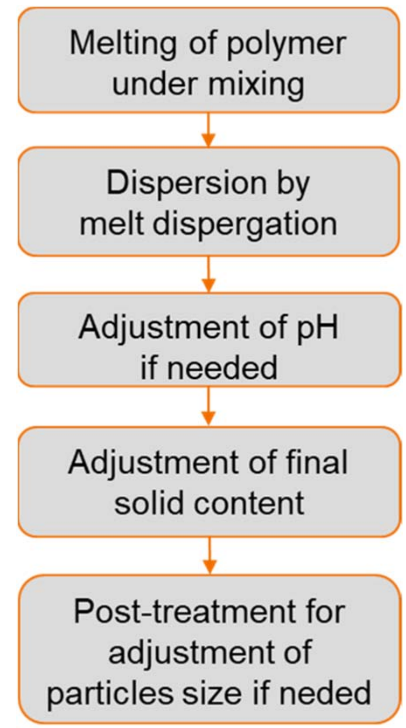


1,4 - butanediol

Thermomechanical method

- Available, scalable, and environmentally feasible, and referred to also as solvent-free extrusion emulsification,
- Exposing a blend of thermoplastic polymer, stabilizer and water to intensive shear forces at elevated temperatures,
- Equipment, process parameters and additives chosen based on the thermal behavior, melt viscosity, and degradation tendency of the polymer. High T_m, for example, requires pressurized equipment,
- Requires that molten polymer has low viscosity for transferring polymer to the aqueous phase under shear during dispersion preparation,
- Used for both bio- and petroleum-based polymers.

Example:



Copolymers and dispersions (not cross-linked)

TYPE 1:

- New monomers for functionality,
- Decreased amount of partially (low) saponified PVOH as a stabilizer.
- Dispersions produced using glass and/or 2L Juchheim reactor.

Copolymer	Mn (g/mol)	Mw (g/mol)	Tg (°C)
1.1	276	1 890	24 ± 1
1.2	1 580	8 280	5.7 ± 0.2
2.1	3 130	21 170	41 ± 0.7
2.2	N.A. in chloroform		28 ± 0.4
2.3	6 200	7 840	39 ± 0.2

TYPE 2:

- New type of monomers,
- Partially saponified PVOH as a stabilizer.
- Polymers / dispersions produced in pilot scale with a Lödige DVT 10L reactor and post-treated.

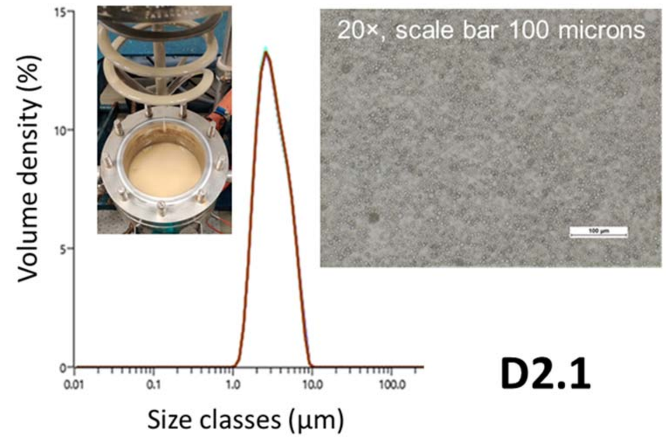
INN PRESSME

https://www.inn-pressme.eu/

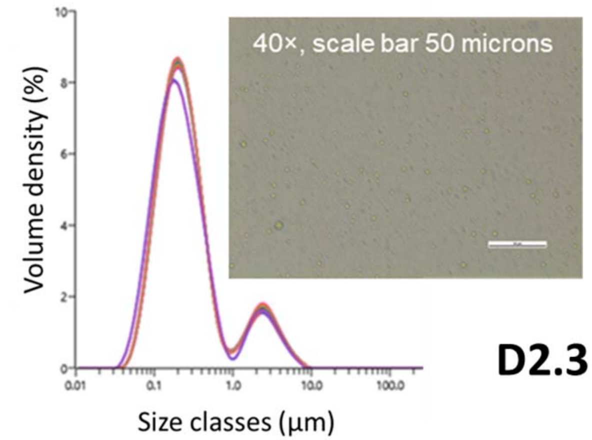
Characteristics of dispersions

CODE	POLYMER	VISCOSITY (100 RPM)	SOLIDS CONTENT	PARTICLE SIZE
D1.1	1.1	150 mPas	29%	2-40 µm
D1.2	1.2	260 mPas	34%	1.5-15 µm
D2.1	2.1	830 mPas	27%	1-10 µm
D2.2	2.2	1100 mPas	40%	1-10 µm
D2.3	2.3	630 mPas	35%	0.04-10 µm

pH of dispersions in the range of 1-3



D2.1



D2.3

Reference polymer dispersions

	CODE	TYPE	CHARACTERISTICS
Conventional	A	Formulated with wax, solids 46%	Hydrophobicity, WVTR
	B	Styrene butadiene, T_g < 15 ˚C	Water vapor barrier
	C	All Acrylic, T_g < 15 ˚C	Oil & grease resistance
Novel type	D	Poly(lactic acid) based, MFFT 20 ˚C	Particle size 1 µm
	E *	Poly(lactic acid) based, MFFT 160 ˚C	Particle size 5 µm
	F	70 : 30 blend of D : E	
	G	Polyethylene based, solids 50%	Water vapor barrier
	H	Polyester based, solids 40%	Water barrier

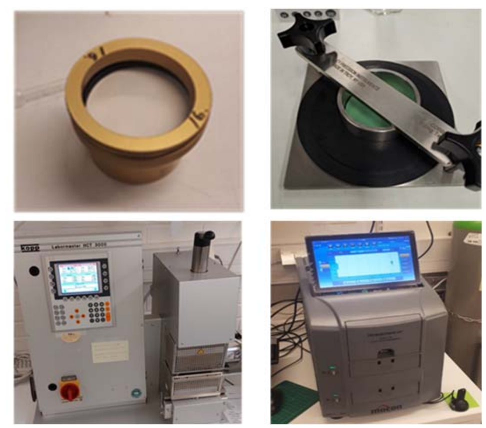
* Tested only in a blend

Laboratory coating

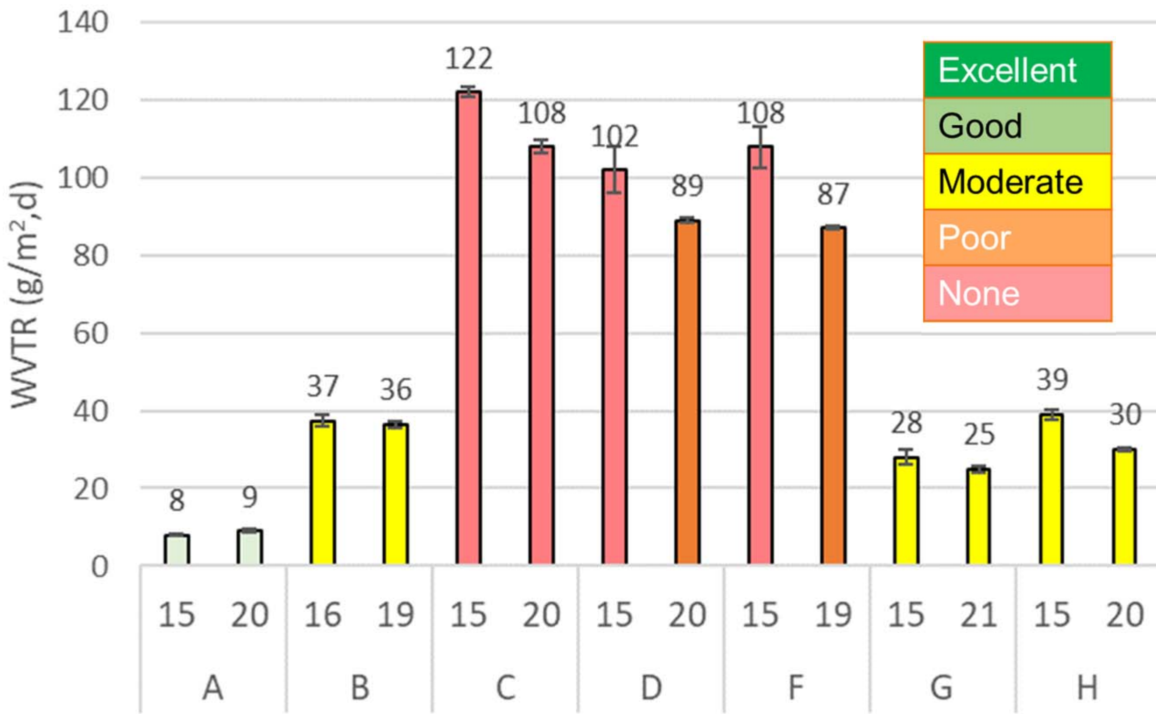
- Two paperboard substrates;
  - Smooth surface of 170 g/m^2 cupstock for prescreening references
  - Coated reverse side of 210 g/m^2 folding boxboard for actual comparison.
- Coating carried out with ERICHSEN lab sheet coater at 50 mm/s,
- Drying performed in an air circulation lab oven at 100 ˚C for 5 min,
- Two target coat weights (15 & 20 g/m^2 and 11-12 & 15-16 g/m^2)
  - Coat weight adjustment with the metering rods and/or by coating solids
- Brookfield viscosity of all coating formulations measured,
- At least 10 sheets coated for each coating and coat weight combination.

Characterization of coated sheets

- Coat weight (g/m^2) – difference in dried uncoated and coated board,
- Pinholes tested with dyed aqueous or alcohol-based liquids,
- Water absorption (g/m^2) during 10 min (ISO 535:2014, TAPPI T-441),
- WVTR (g/m^2/d) at 23 ˚C / 50% RH and 38 ˚C / 90% RH (ASTM F1249−13),
- OTR (cm^3/m^2/d) at 23 ˚C / 0% RH (ASTM D3985),
- KIT test for OGR (TAPPI T-559),
- Grease and oil barrier (VTT Method),
- Hexane vapor transmission rate HVTR (g/m^2/d),
- Heat sealability with visual ranking,
- SEM imaging.



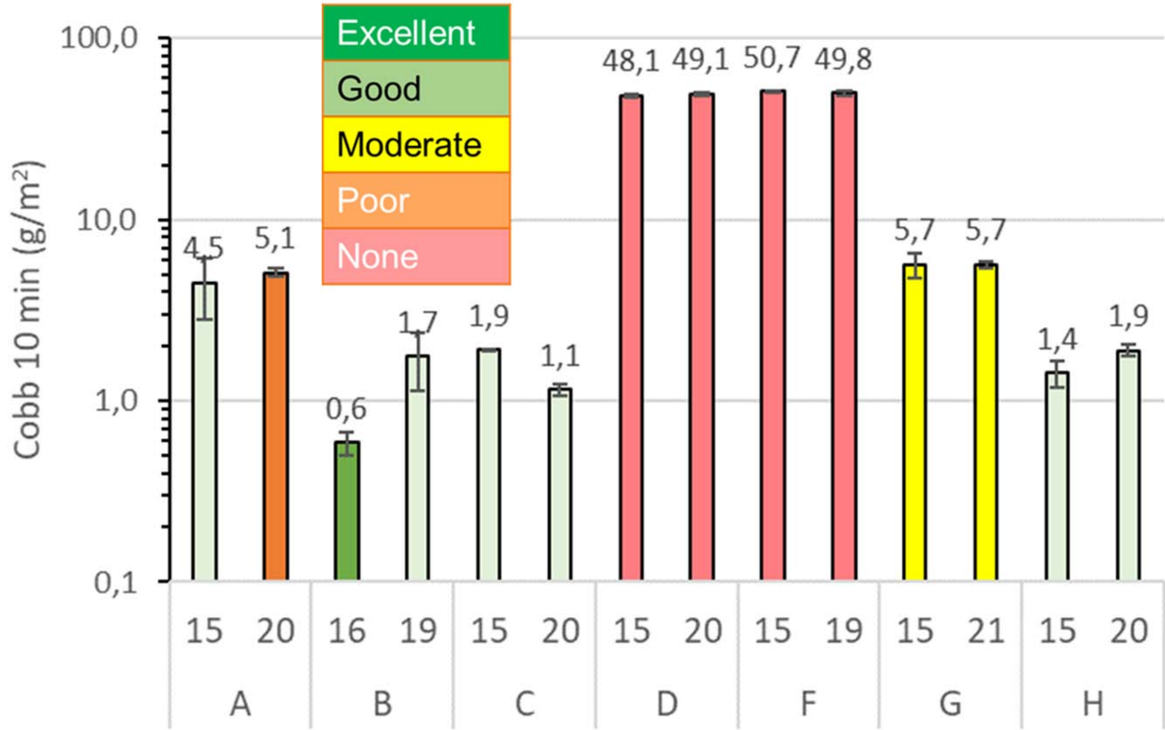
Water vapor barrier at 50% RH and 23 ˚C



Base board could not be measured

- Dispersions intended for WV barrier had good to moderate barrier, and the best WVTR with wax formulated dispersion A,
- No clear correlation between water and water vapor barrier,
- PLA-based reference coatings performed slightly better than C,
- Increasing coat weight typically decreased WVTR, although the impact was not significant.

Water absorption after 10 minutes



Base board 46 ± 0,3 g/m²

- Some references good or even excellent water barriers.
- PLA references D and F did not form barrier at these drying conditions and coat weights,
- Above certain coat weight no obvious correlation with barrier performance,
- A limited number of defects (B) do not necessarily destroy water barrier.

Grease and oil barrier

Base board immediate staining

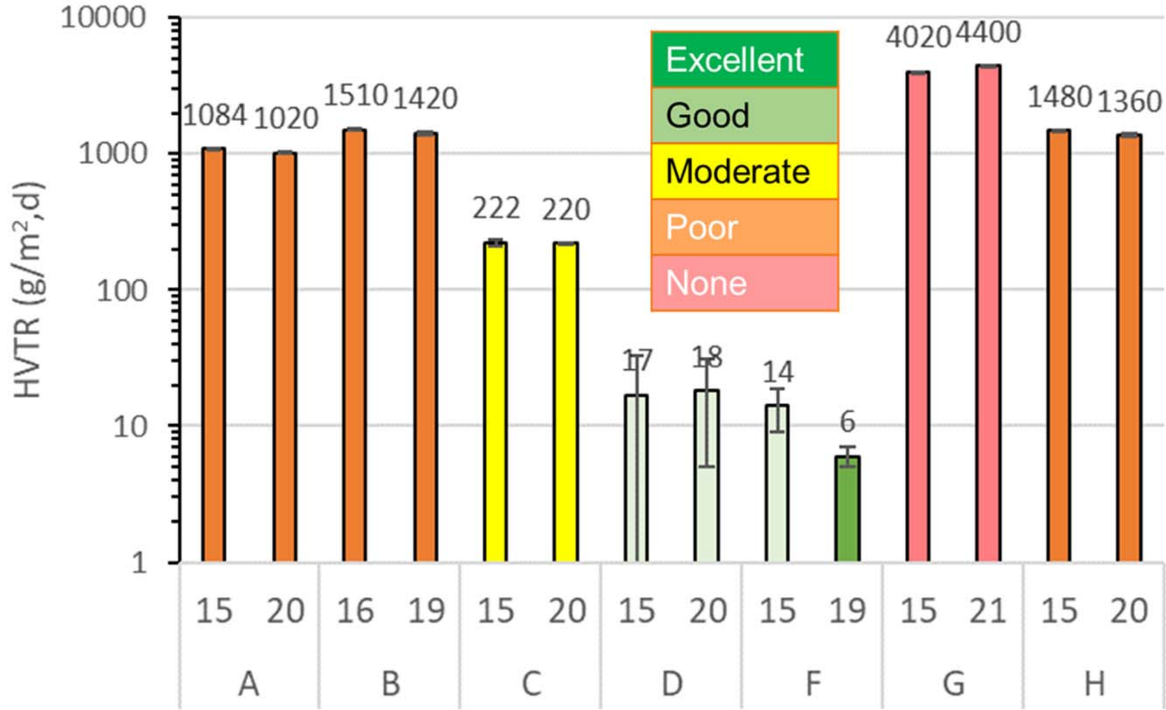
Coating	g/m^2	Breakthrough time *
A	15 & 20	**6-24 HOURS**
B	16	**< 1 HOUR**
	19	**6-24 HOURS**
C	15 & 20	**> 1 WEEK**
D	15	**3-4 DAYS**
	20	**> 1 WEEK**
F	15 & 19	**> 1 WEEK**
G	15 & 21	**1.25-2 DAYS**
H	15 & 20	**6-24 HOURS**

* Breakthrough when at least two out of five pieces show ≥ 1% stained area

Excellent
Good
Moderate
Poor
None

- Dispersion intended for grease barrier (C) and PLA based coatings (D,F) excellent barriers,
- Dispersions intended for water and/or water vapor barrier were at best moderate grease barriers,
- Grease barrier is sensitive to coating defects, which explains partly the poor performance of e.g. B

n-Hexane vapor (mineral oil) barrier



- PLA based dispersions D and F provided the best barrier against n-hexane vapor,
- C with good grease barrier had better performance than the other two conventional dispersions A and B,
- PE based G as a polyolefin was the poorest barrier against n-Hexane

Base board 7840 ± 70 g/(m^2,d)

Prescreening of reference dispersions

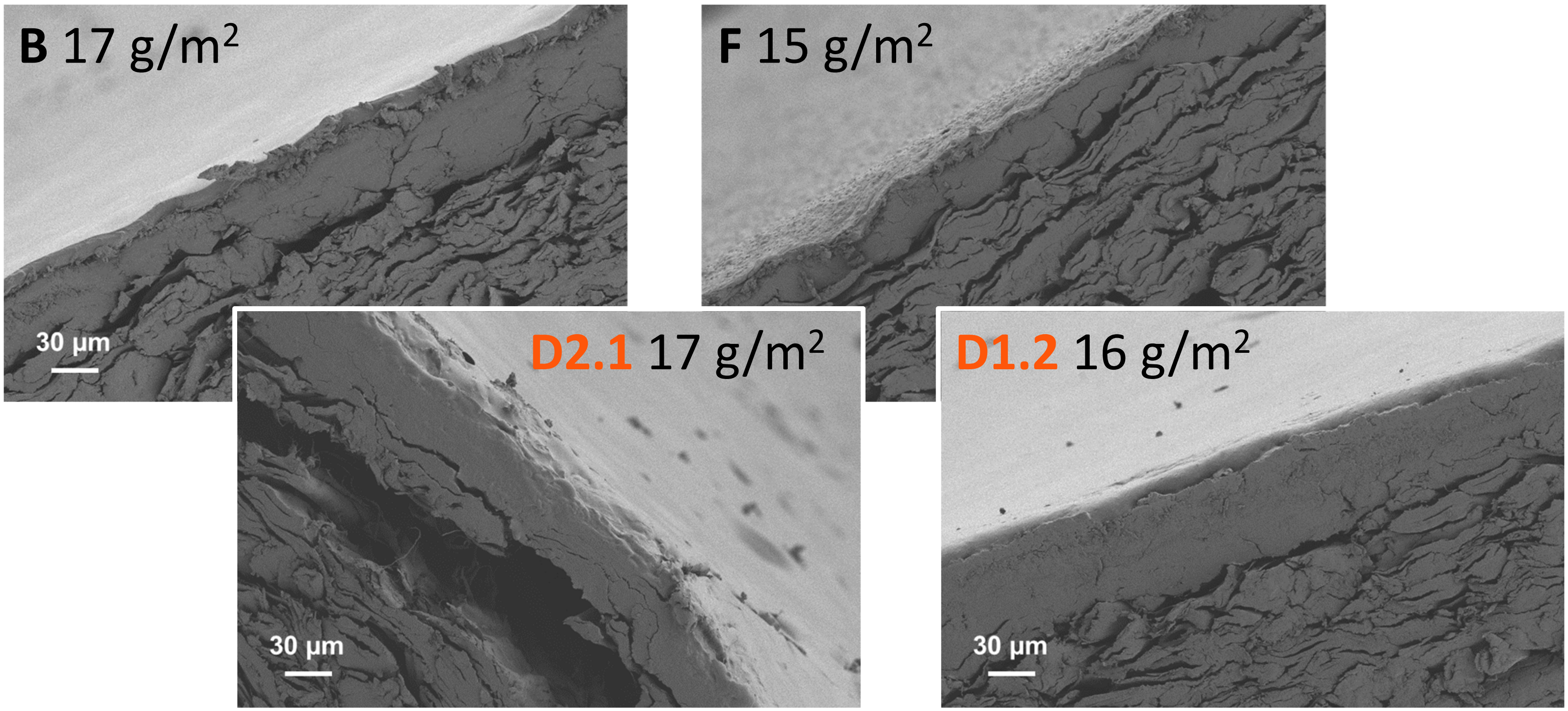
++	Good / Excellent
+	Moderate
0	Poor / None

	WATER	WATER VAPOR	N-HEXANE	GREASE	OXYGEN	SEALING
A	**++/+**	**++**	0	+	0	**YES**
B	**++**	+	0	+/0	0	YES *
C	**++**	0	+	**++**	0	**YES**
D	0	0	**++**	**++**	0	**YES**
F	0	0	**++**	**++**	+	**YES**
G	+	+	0	**++**	0	**YES**
H	**++**	+	0	+	0	YES *

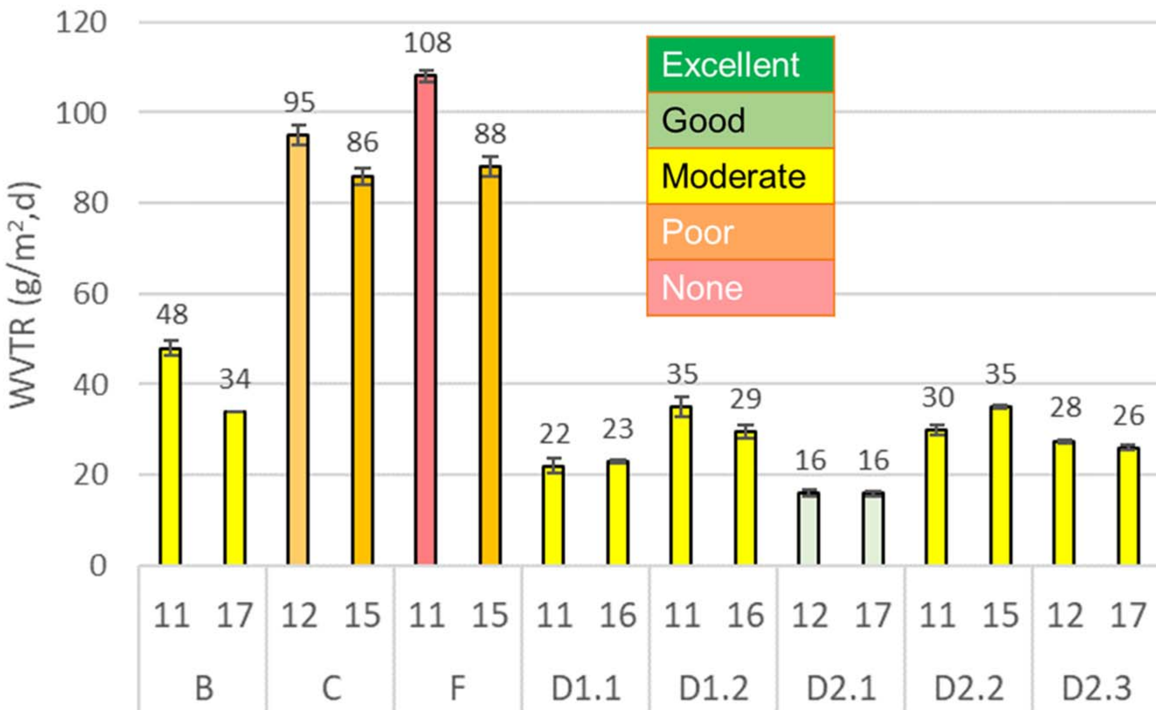
(highlighted rows B, C, F) **Chosen for comparison with experimental dispersions**

* Blocking tendency

Uniform poly(lactic acid) copolymer coatings



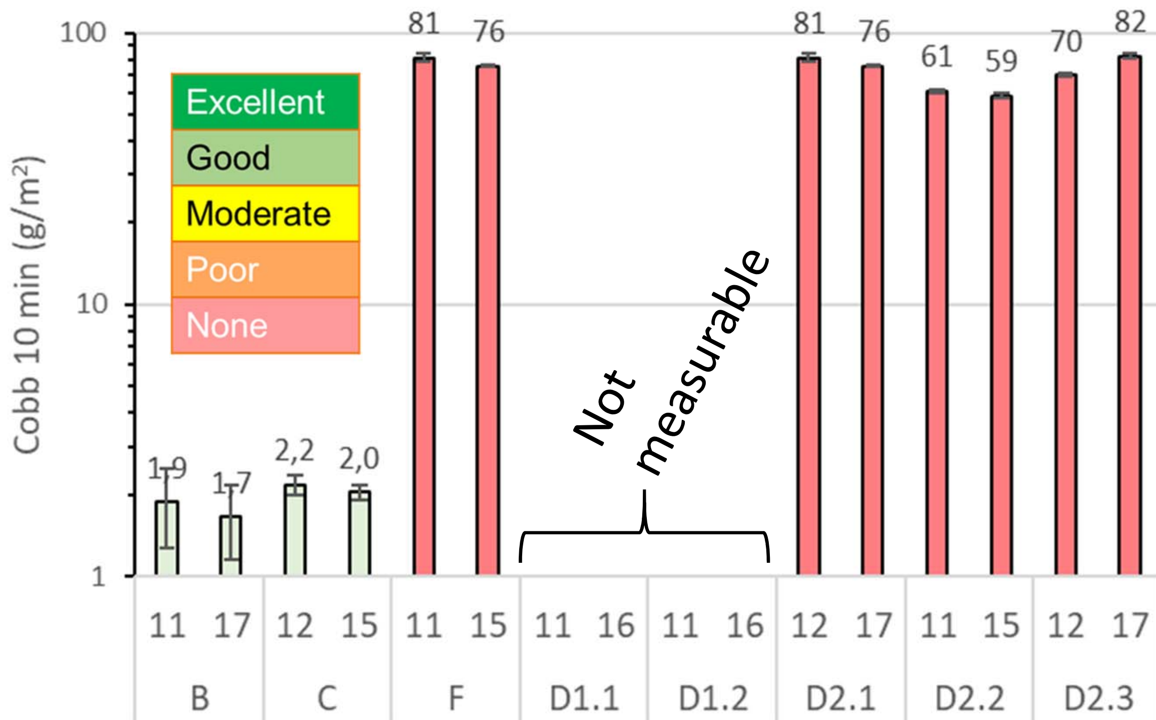
Water vapor barrier at 50% RH and 23 ˚C



Base board 250 ± 10 g/(m²,d)

- Better than the reference PLA and similar/better than dispersion B,
- D2.1 the best (TYPE 2), and D1.1 better than D1.2 (TYPE 1),
- At tropical conditions TYPE 1 dispersions performed better than TYPE 2, but the values in general were significantly higher than with dispersion B likely due to PVOH used as a stabilizer.

Water absorption after 10 minutes



Base board 110 ± 1 g/m²

- B and C provided similar values also at lower coat weight with this substrate,
- Poly(lactic acid) dispersions - similarly to the reference F – had limited impact on barrier,
- TYPE 1 dispersions coatings could not be measured as the board delaminated, which is likely due to a more soluble PVOH and a low molecular weight polymer.

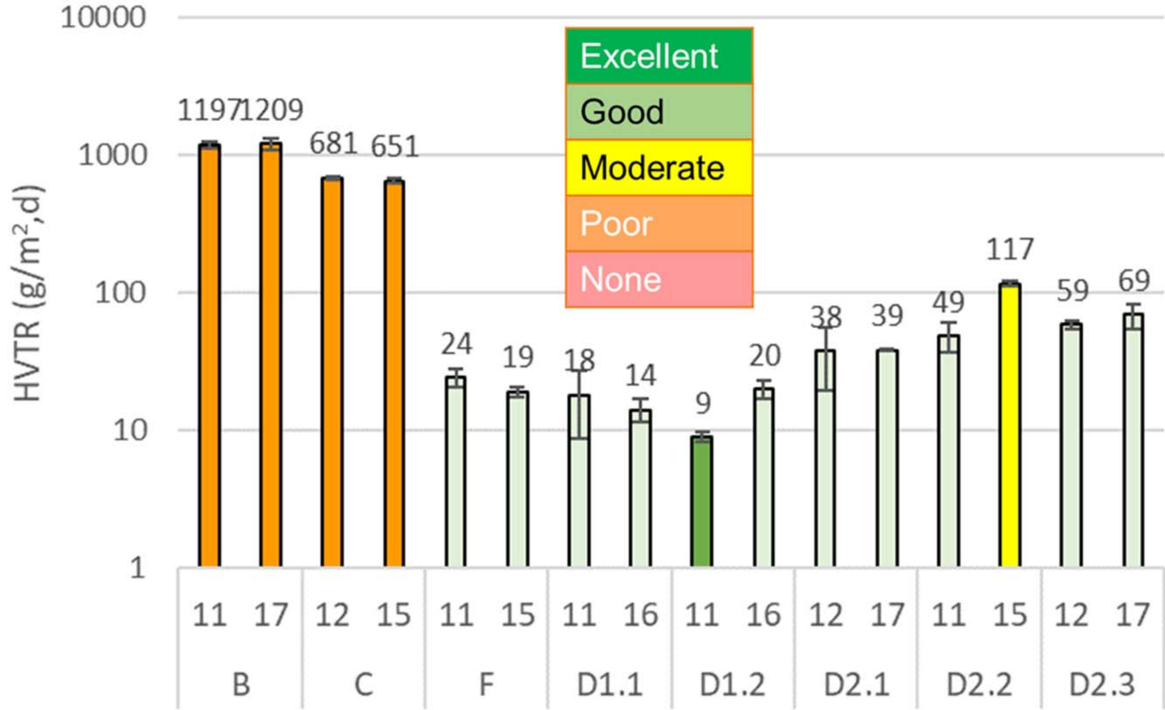
Grease and oil barrier

Coating	g/m^2	Breakthrough time *
B	11	3-4 DAYS
	17	4-7 DAYS
C	12 & 15	> 1 WEEK
F	11	6-24 HOURS
	15	> 1 WEEK
D1.1	11 & 16	> 1 WEEK
D1.2	11 & 16	2-3 DAYS
D2.1	12 & 17	> 1 WEEK
D2.2	11	> 1 WEEK
	15	4-5 DAYS
D2.3	12	3-4 HOURS
	17	5-6 HOURS

Excellent
Good
Moderate
Poor
None

- Dispersion C and most of the poly(lactic acid) dispersions were good barriers without staining even after one week,
- D2.1 had also maximum KIT value (12) at both coat weights,
- In spite of some scatter between the individual test pieces, D2.3 was poor barrier, and D1.2 was somewhat poorer than D1.1,
- Several new copolymer dispersions, however, provided better barrier than the reference F at low coat weight.

n-Hexane vapor (mineral oil) barrier

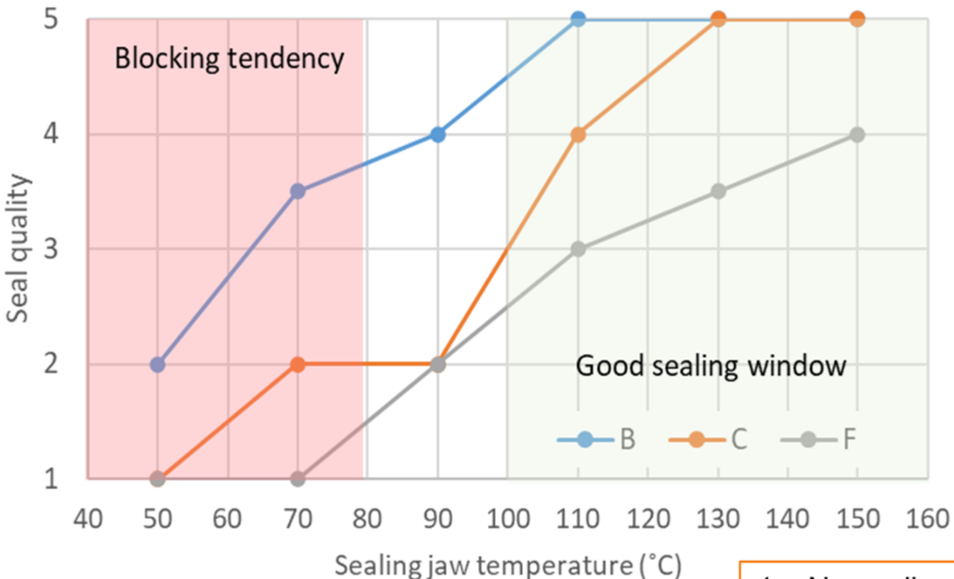


Base board 1200 ± 70 g/(m²,d)

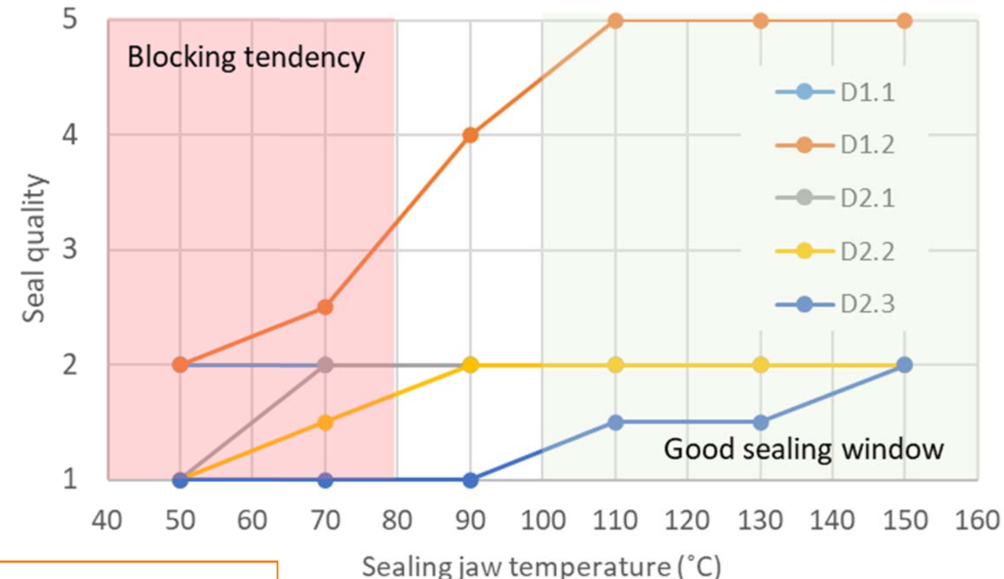
- Both the PLA reference F and all the new dispersions performed better than the conventional references,
- TYPE 1 versions were on average similar to the reference F and better than TYPE 2 dispersions,
- Among the TYPE 2 dispersions D2.1 was slightly better than D2.2 or D2.3.

Heat sealing (higher coat weight)

Reference dispersions



Novel lactic acid-based dispersions



1 – No sealing
2 – Weak seal (with sound)
3 – < 50% seal area damaged
4 – ≥ 50% seal area damaged
5 – complete damage (in board)

Settings: 200 N and 1.5 s
Coating against coating.

Performance of different dispersions

++	Good / Excellent
+	Moderate
0	Poor / None

	WATER	WATER VAPOR	N-HEXANE	GREASE	OXYGEN	SEALING
B	++	+	0	++	0	+ *
C	++	0	0	++	0	++
F	0	0	++	++/+	0	++
D1.1	0	+	++	++	0	0
D1.2	0	+	++	++	0	+ *
D2.1	0	++	++	++	0	0
D2.2	0	+	++/+	++	0	0
D2.3	0	+	++	0	0	0

* Blocking tendency

Conclusions

- Poly(lactic acid) copolymer dispersions with solids content up to 40% produced;
  - Production of polymers and dispersions upscaled from lab to pilot scale,
  - Post treatment (filtration, mechanical treatment) can have positive impact on particle size,
- Performance to be optimized with copolymer composition and additives, and a precoated substrate recommended for optimal coating quality,
- Tested non-crosslinked dispersions feasible for dry and greasy products;
  - Excellent oil and grease resistance and a good barrier against mineral oil migration,
  - Water vapor barrier at 50% RH comparable to a dispersion designed for WP barrier,
  - Applications with a direct water contact or high humidity challenging,
  - None of the dispersions (including references) provided true oxygen barrier,
- Heat sealing performance to be improved;
  - Dispersion from a low T_g copolymer indicated the possibility for adjusting heat sealability,
- Findings to be verified in pilot scale.

Packaging concepts and demonstrations

PLA DISPERSION
FIBRIL. CEL. COAT.
PLA DISPERSION
BASE PAPER

~ 38 g/m² (PLA dispersion / fibril. cel. coat. / PLA dispersion)

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Kumar, Vinay, 18th Biennial TAPPI European PLACE Conference | 10-12 October 2022

PLA DISPERSION
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BASE PAPER

< 10 g/m² (PLA dispersion / BioORMOCER® / PLA dispersion)

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Open Innovation Test Bed

Koppolu, R., Nissinen, E., Hämäläinen, R, et al., Specialty Papers Europe | 5-6 September 2023

THANK YOU
Questions or other remarks?

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