Recyclable all-thermoplastic composites by TP-RTM

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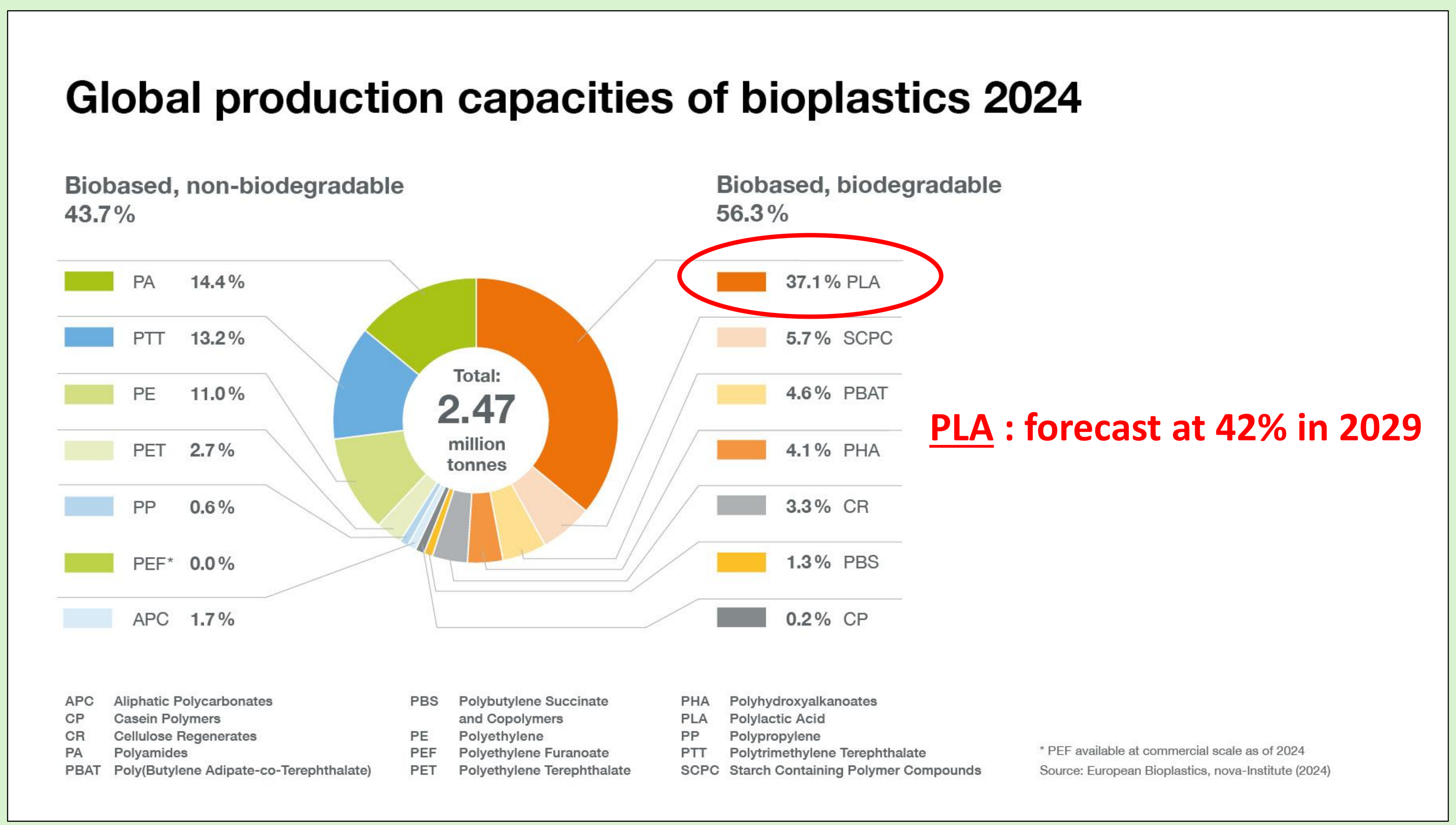
Context[1]



Global production capacities of bioplastics expected at 5,73 million tonnes in 2029

Problematics & objectives

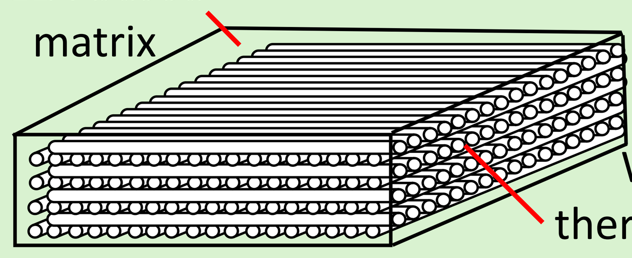
PLLA is:

- Biobased
- Biocompatible
- Compostable under industrial conditions

- Low glass transition temperature ($T_g \approx 60$°C)
  ⮡ Loses its shape under heat
- Low elongation at break ($\varepsilon_B \approx 4$-6%)
  ⮡ Brittleness[2]

- Reinforcement of PLLA by producing composite materials[3]
- Copolymerization of L-lactide (L-LA) with ε-caprolactone (ε-CL): impact resistance and shape recovery
- Thermoplastic Resin Transfer Molding (**TP-RTM**) Process: one step process via *in situ* polymerization of the matrix, good wettability matrix/reinforcement, high reinforcement ratios, control of the thickness of the produced part

Produce recyclable all-thermoplastic composites

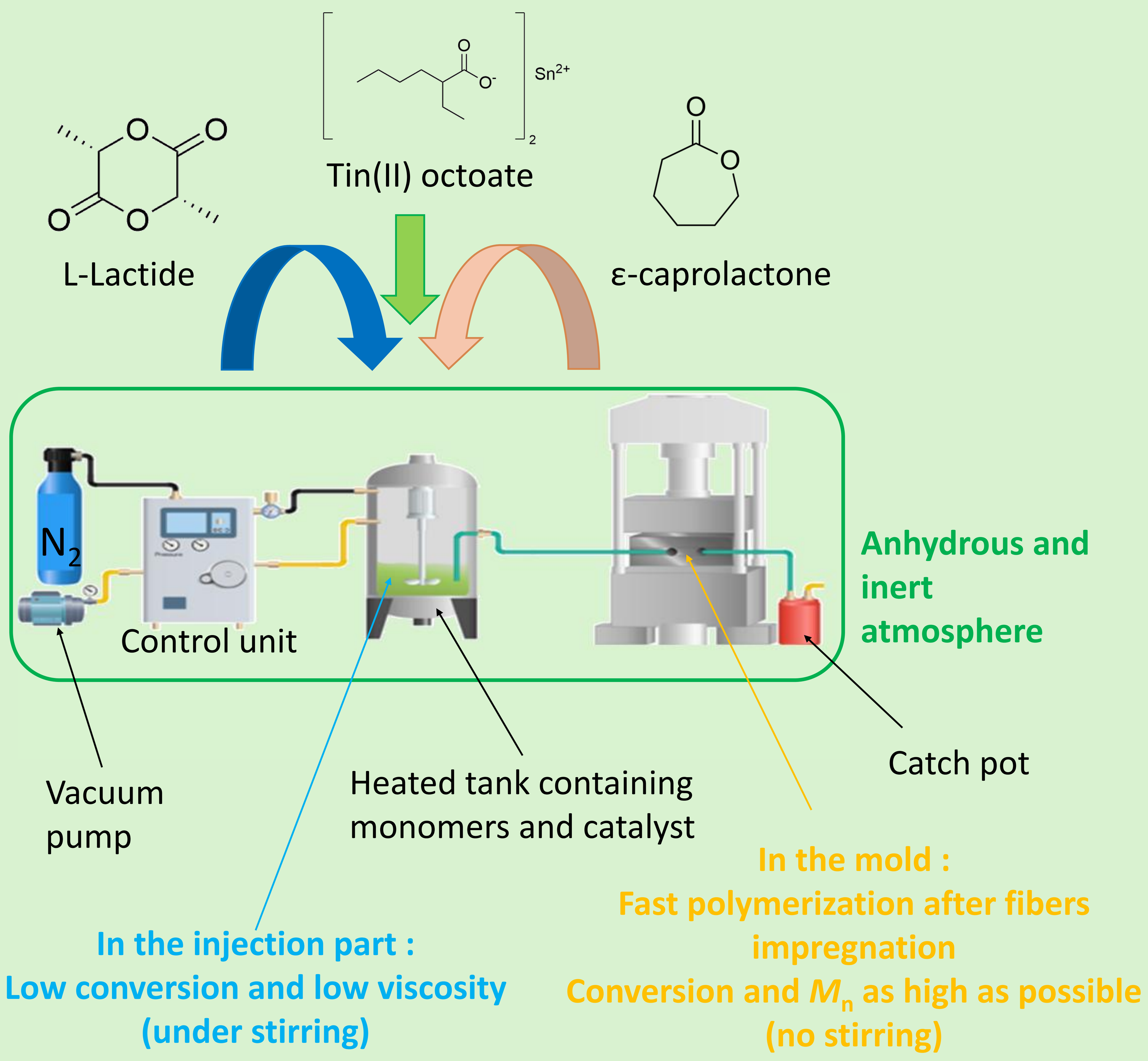


Locks:

- Quantitative conversion of monomers
- High molar masses (M_w > 100,000 g/mol) for high mechanical properties
- Good fiber/matrix cohesion
- Working under inert atmosphere
- Avoid reinforcement-catalyst interaction, shrinkage and movement of the reinforcement
- Minimizing porosity in composites

Methodology

Single tank TP-RTM apparatus used in this study [4]

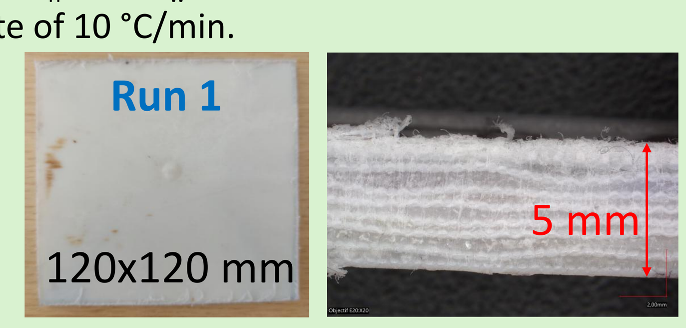


Results

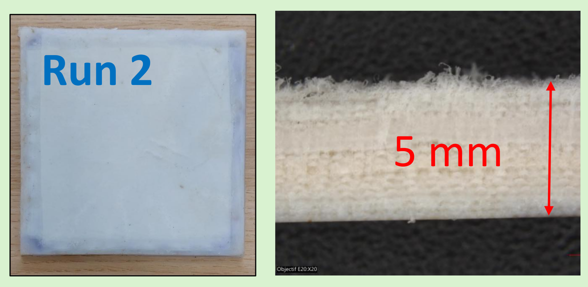
Poly(L-lactide) (PLLA) and poly(L-lactide-co-ε-caprolactone) (PLCL)/thermoplastic fabric composites by TP-RTM [a]

Run	Mold temperature (°C)	Polymerization time (h)	Conversions [b] (%)		M_n [c] (g/mol)	M_w [c] (g/mol)	Đ	T_g [d] (°C)	T_f [d] (°C)
			L-LA	ε-CL					
PLLA/thermoplastic fabric composites									
1	160	3	95	-	122,200	163,100	1.33	57	175
2	185	2	97	-	99,300	144,200	1.45	55	175
PLCL/thermoplastic fabric composites									
3	160	5	97	79	20,900	40,600	1.94	21	138
4	160	7	96	87	50,700	108,800	2.14	22	139
5	185	5	94	92	23,900	47,200	1.98	20	-

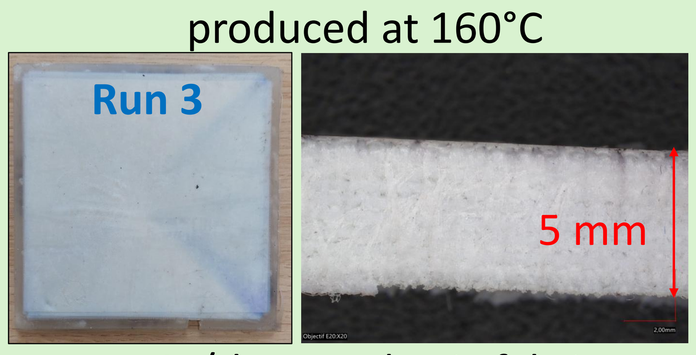
[a] Experimental conditions: PLLA = poly(L-lactide), PLCL = poly(L-lactide-co-ε-caprolactone), L-LA = L-lactide, ε-CL = ε-caprolactone, catalyst = $Sn(Oct)_2$, ([L-LA] +[ε-CL])/[Sn] = 2000. [b] Determined by ^1H NMR in $CDCl_3$. [c] Determined by SEC in $CHCl_3$ at 1 mL/min and 25°C for runs 1 and 2, in THF at 1 mL/min and 35°C for runs 3, 4 and 5. Correction coefficient for M_n and M_w : 0.68 for runs 1 and 2, [0.58 x wt % LA + 0.56 x wt % CL] for runs 3, 4 and 5. [d] Determined by DSC with a rate of 10 °C/min.



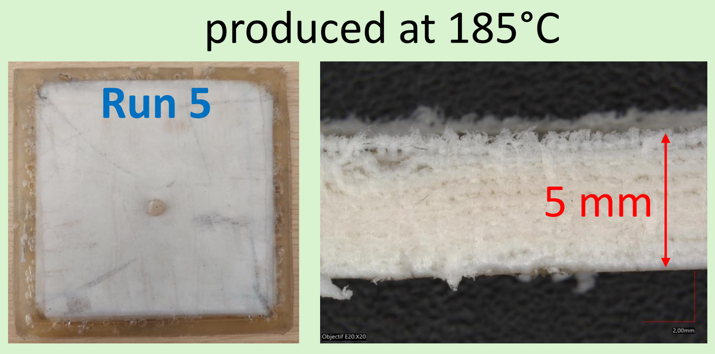
PLLA/thermoplastic fabric composite produced at 160°C



PLLA/thermoplastic fabric composite produced at 185°C



PLCL/thermoplastic fabric composite produced at 160°C



PLCL/thermoplastic fabric composite produced at 185°C

L-LA conversions superior to 94% for PLLA and PLCL matrices composites no matter the processing temperature. ε-CL conversions up to 92% could be reached with a processing temperature of 185°C, 160°C is not enough in these conditions to get an acceptable ε-CL conversion. M_w as high as 163,000 g/mol have been reached for the PLLA matrix composites versus 108,800 g/mol for the PLCL matrix ones. No mesovoids could be observed in these composites.

Conclusion & Outlooks

Following previous works conducted at UMET[5,6,7]:

- first prototypes of **all-thermoplastic** composites produced by **TP-RTM**
- both PLLA homopolymer and PLLA-based copolymer matrices used
- first production by *in situ* polymerization of fully thermoplastic composites
- quasi quantitative conversion of L-lactide
- conversion of ε-caprolactone to improve (temperature and heating time)
- study of the recycling of PLLA/thermoplastic fabric composites in progress

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References

1. https://www.european-bioplastics.org/bioplastics/materials/
2. Jamshidian, M.; Tehrany, E. A.; Imran, M.; Jacquot, M.; Desobry, S. Poly-Lactic Acid: Production, Applications, Nanocomposites, and Release Studies. *Compr. Rev. Food Sci. Food Saf.* 2010, *9* (5), 552–571. https://doi.org/10.1111/j.1541-4337.2010.00126.x.
3. Murariu, M.; Dubois, P. PLA Composites: From Production to Properties. *Adv. Drug Deliv. Rev.* 2016, *107*, 17–46. https://doi.org/10.1016/j.addr.2016.04.003.
4. Miranda Campos, B.; Bourbigot, S.; Fontaine, G.; Bonnet, F. Thermoplastic Matrix-based Composites Produced by Resin Transfer Molding: A Review. *Polym. Compos.* 2022, *43* (5), 2485–2506. https://doi.org/10.1002/pc.26575.
5. Louisy, E. Synthèse de composites à matrice polylactide par procédé RTM (Resin Transfer Molding). Thèse de l'Université de Lille, 2019.
6. Miranda Campos, B. Copolymer-based PLLA matrix composites produced by TP-RTM. Thèse de l'Université de Lille, 2023.
7. Miranda Campos, B.; Beauvois, J.; Bourbigot, S.; Fontaine, G.; Stoclet, G.; Bonnet, F. *Polym. Compos.* 2024