Poly(L-lactide-co-ε-caprolactone)-matrix composites produced in one step by *in situ* polymerization in TP-RTM

Bernard Miranda Campos,(1) Gaëlle Fontaine,(1) Serge Bourbigot,(1,2) Grégory Stoclet(1) and Fanny Bonnet.*(1)

(1) Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000 Lille, France.
(2) Institut Universitaire de France (IUF), France.
*e-mail to: fanny.bonnet@univ-lille.fr

Abstract: Poly(L-Lactide) (PLLA) is a semi-crystalline biopolymer of great interest due to its biosourced, biocompatible and compostable nature. However, its brittleness prevents its use in a wide range of applications. In order to reinforce PLLA, it is often used in polymer blends or in composites. In this contribution, an unprecedented family of PLLA-based / glass fabrics composites with poly(L-lactide-co-ε-caprolactone) statistical copolymers as the matrix is reported. These biocomposites were produced in one step synthesis by *in situ* copolymerization of L-lactide and ε-caprolactone in Thermoplastic Resin Transfer Molding (TP-RTM) process. These materials display high matrix/fabrics wettability along with strong rubbery character.

Keywords : Polylactic acid, biocomposites, TP-RTM, ε-caprolactone, thermoplastic copolymer matrix, glass fabrics.

Polylactic acid, commonly called polylactide, is a biobased, biocompatible, compostable and degradable *in vivo* biopolymer involved in numerous applications including biomedical and packaging.[1,2] Poly(L-Lactide) (PLLA), arising from the homopolymerisation of L-lactide isomer, is an isotactic semi-crystalline biopolymer of great interest displaying good mechanical properties that could allow its use as an alternative to some common polyolefines. However, PLLA is quite brittle (elongation at break of 2-6 %) what prevents its use in a wide range of applications, in particular for long-life objects such as transportation or sport equipment among others. In order to overcome this issue, PLLA is often used in blends with other polymers[3,4] or in composites materials.[5]

Another way to tune the thermal and mechanical properties of PLLA, is to copolymerize L-lactide with other cyclic esters, and in particular with lactones displaying properties able to overcome PLLA weaknesses.[6,7] For example, ε-caprolactone is one of the lactones often copolymerized with lactide,[8,9] as poly(ε-caprolactone) (PCL) exhibits an elongation at break up to 300 times superior (314%)[10] to that of PLLA (2-6%). However, the statistical copolymerization of these two monomers is quite tricky as the oxophilic metal-based catalysts involved in these reactions by Ring Opening Polymerization (ROP) will preferentially coordinate and insert lactide monomer, resulting in the formation of pure PLLA or block copolymers.[9] Thus, in order to reach statistical lactide-lactone copolymers, chemists can either design specific metal-based catalysts,[9] or either play on experimental conditions, such as reaction time and temperature, to increase the occurrence of intermolecular transesterification reactions, allowing the random distribution of the monomers in the macromolecule chain.[11]

As mentioned above, the production of composites is one of the most common way to reinforce PLLA.[5] Actually, composite materials display many advantages over traditional materials, whether in terms of lightness or mechanical and chemical resistance. The development of composites meets the requirements of industrial markets for applications in the fields of transportation and construction, as well as sports and leisure. In a context of sustainable development, a growing number of works relate to the production of composites with bio-based matrices including polylactide.[12] Among composites production processes, Resin Transfer Molding (RTM) is a specific process which relies on the injection, into a mold containing fabrics, of a monomer and a catalyst in order to carry out the *in situ* polymerization of the matrix (Figure

1).[13] The major advantage of RTM over conventional melt processes is the possibility of reaching a high amount of fabrics while improving its wetting by the matrix. While a wide selection of thermosetting matrix resins are available on the market for RTM process, there are only a few commercial resins for thermoplastic matrices.[14,15,16] It should be noted that in the latter case, the RTM process is called Thermoplastic-RTM (TP-RTM).

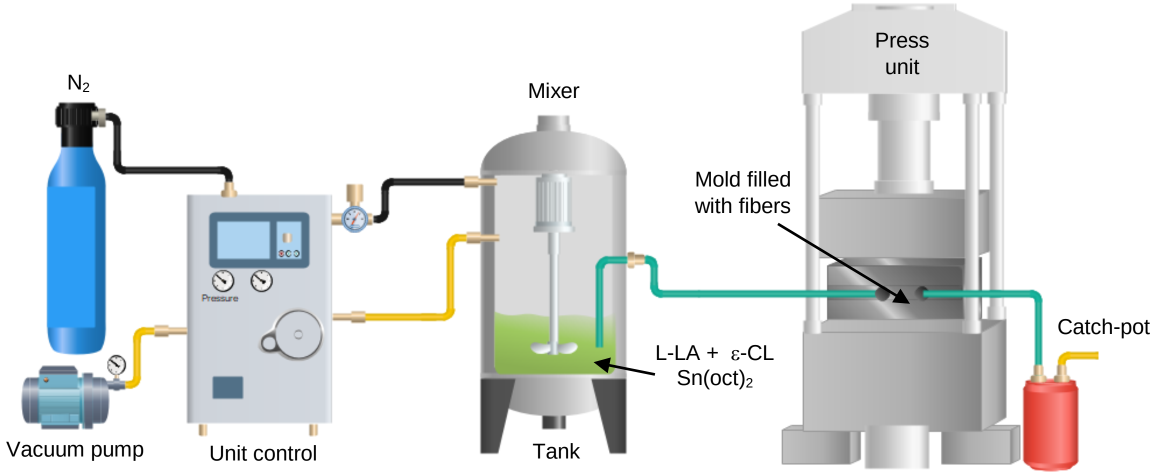

Figure 1: Scheme of Resin Transfer Molding (RTM) process for a single component apparatus

Although work has been carried out in TP-RTM with ε-caprolactone, which is a monomer liquid at room temperature,[17,18] composites with a polylactide matrix elaborated via this process had never been described, due to the lock linked to the solid state of this monomer at RT. Indeed, TP-RTM process is generally composed of one tank (two tanks can be used in some specific cases) where the monomer and catalyst are mixed before their injection in a mold containing the reinforcement (Figure 1). In the specific case of L-lactide, an additional step is necessary where the monomer is melted at high temperature (above 100°C). Thus, this will initiate the polymerization and increase the viscosity of the reaction medium, which can be a major lock regarding the injection step and the fabrics impregnation. Recent work carried out by our team made it possible to obtain the first prototypes of PLLA / glass fabrics composites with different reinforcement rates.[19] In the present work, we aimed at strengthening the PLLA matrix by producing an unprecedented family of composites based on statistical poly(L-lactide-co-ε-caprolactone) copolymers as the matrices, by *in situ* copolymerization of L-LA with ε-caprolactone in TP-RTM process. Poly(L-lactide-co-ε-caprolactone) / fabrics composites have never been reported by any other composite process. To date, only nanocomposites involving this copolymer matrix were reported.[20,21,22]

Regarding the fact that tin octoate is an efficient ROP catalyst of L-lactide in reactive extrusion[23] and based on our previous study on PLLA / glass fabrics composites by TP-RTM,[19] the latter was used as the catalyst in the present work. Moreover, tin octoate is known to be able to copolymerize L-LA with ε-CL in bulk conditions.[7,8] Preliminary studies of bulk copolymerizations at the gram scale were conducted and are reported in the SI (table S1). The objective was to determine the best experimental conditions (*i.e* monomer over catalyst ratio and composition of co-monomers in the feed) to be used in the TP-RTM. Actually, the main lock regarding the copolymerization reaction in TP-RTM process is related to the different physical state of both monomers, L-LA being a solid at RT while ε-CL is a liquid. This could be an issue as the reaction is conducted in a single tank TP-RTM machine where all the reagents are mixed together. In these conditions, the catalyst could react directly on ε-CL during the melting phase of L-LA, leading to the increase of the viscosity medium and preventing the injection step. The preliminary studies conducted at small scale in flasks, showed that the viscosity of the media after 30 min at 150°C (*i.e.* for experimental conditions corresponding to the melting step of L-LA in TP-RTM process) was still water-like, and thus low enough to potentially allow the injection of the mixture in the RTM mold. Moreover, these tests highlighted that high conversions of both monomers could be reached with 2000 equiv. of co-monomers (see Table S1 in the SI). Based on these observations, poly(L-lactide-co-ε-caprolactone) / glass fabrics composites were then prepared using a DIATEX TP-RTM machine. L-LA, ε-CL (200 g of monomers in total) and tin octoate (all used without any purification) were mixed together in the tank, and heated at 150°C for 30 min to allow the melting of L-LA. The mixture was then stirred for 2 min and injected in a pre-heated mold under press at 185°C containing 10 layers of woven glass fabrics (corresponding to 45-49 wt% in the final composite) where the polymerization takes place (see SI, experimental section). The reaction was conducted with various amounts of ε-CL monomer ranging from 0 to 30 mol%. Table 1 summarizes the experiments related to the synthesis of poly(L-Lactide) and poly(L-lactide-co-ε-caprolactone) / glass fabrics conducted by TP-RTM. For the sack of comparison with new statistical copolymer-matrix composites, a pure PLLA / glass fabrics composite was produced with the same experimental conditions as previous work (2000 equiv. L-LA, 185°C, 2h) and is reported in table 1 as run 1. In the former study, the optimal L-LA monomer over catalyst ratio to reach the highest conversion and molar mass was found to be 2000 equivalents.[19] In that frame, and regarding the preliminary copolymerization results at small scale, the same monomer over tin ratio was used for the first copolymerization experiment conducted with 10 mol % of ε-CL in the initial feed (Table 1, run 2). The viscosity of the reaction medium after the melting step of L-LA at 150°C for 30 min was still water-like and thus suitable for the injection step, indicating that the tin catalyst did not react directly on the ε-CL liquid monomer. This point was confirmed by ^{1}H NMR analysis of the mixture residue in the tank just after injection, showing that no ε-CL was converted at that stage and that only 6 % of L-LA was converted to PLLA. This indicates that even if L-LA is solid, the tin catalyst will always coordinate and insert this monomer first, as observed in solution polymerization. After injection, the polymerization time was set up to 5 h, instead of 2 h for pure L-LA, in order to reach complete conversions of both monomers, as the competition between the two co-monomers slower the polymerization kinetics. At the end of the reaction, nearly full conversions of both monomers were reached with 96 % and 94 % for L-LA and ε-CL respectively. The resulting copolymer matrix display high molar masses of 71100 g.mol^{-1} along with narrow dispersity of 1.27 and ratios of co-monomers in the final matrix close to the 90/10 initial feed ratio (some of the co-monomers / catalyst mixture stays at the bottom of the tank after injection due to the process itself which could result in a variation of the composition of the final polymer). By view of the positive result obtained for the first run involving ε-CL as co-monomer, the molar ratio of lactone was then double and set up to 20 mol% (run 3). Full conversions of both co-monomers were reached again with 97 and 96 % for

L-LA and ε-CL respectively. The M_n of the resulting matrix reached 43200 g.mol^{-1}, still with narrow dispersity of 1.42.

The effect of the monomer over catalyst ratio on the conversions and the molar masses was investigated for the monomer feed involving 20 wt% of ε-CL. Reactions were conducted with 3000 and 4000 equivalents of co-momoners *vs* tin with the same reaction time of 5 h (runs 4 and 5). At 3000 equivalents, full conversions of both monomers were still reached and the molar masses could be increased up to 51600 g.mol^{-1} with narrow dispersity of 1,37 (run 4). When decreasing the tin concentration in the reaction medium, *i.e* with 4000 equiv. of co-monomers, the ε-CL conversion went down to 89 % while the L-LA conversion remained complete (run 5). Moreover, no significant impact was observed on the molar mass of the resulting composite matrix (52200 *vs.* 51600 g.mol^{-1}, run 5 *vs* 4). The best monomers over catalyst ratio to reach full conversions along with high molar masses of the resulting matrix is thus 3000 equivalents.

The copolymer matrices composition was examined by ^{1}H NMR analysis. The integrations of the signals related to the methine group of L-LA and those of methylenes of ε-CL were used to calculate the compositions. The Bernoullian model, which is commonly used to determine the microstructure of the copolymers was chosen to study the nature of the copolymers.[24] In equations 1 to 3, (LA) and (CL) are the comonomer molar fractions and (LA-CL) is the average dyad molar fraction. The number-average sequence lengths of LA (I_{LA}) and CL (I_{CL}) and the Bernoullian random-number average sequence lengths are show in Equation 1 and Equation *2* respectively. The randomness character (R) (Equation 3) presume the type of copolymer sequence. When R is close to 1, the copolymer exhibits a random or alternating sequence, while it has a rather blocky structure when R is close to 0. All the microstructure parameters arising from these calculations are reported in table 1.

Equation 1 $$\mathrm{I}_{\mathrm{LA}} = \frac{2\,(LA)}{(LA-CL)} \quad \mathrm{I}_{\mathrm{CL}} = \frac{2\,(CL)}{(LA-CL)}$$

Equation 2 $$(\mathrm{I_{LA}})_{\mathrm{random}} = \frac{1}{(CL)} \quad (\mathrm{I_{CL}})_{\mathrm{random}} = \frac{1}{(LA)}$$

Equation 3 $$\mathrm{R} = \frac{(LA-CL)}{2(LA)(CL)}$$

From these microstructure parameters, one can observe that all copolymer matrices synthetized in this work via TP-RTM showed a random nature, with R above 0.8 for all samples. The experimental conditions seem to favor the intermolecular transesterification reactions, leading to the random character of the resulting copolymer matrices. Actually, it is well known that these secondary reactions are enhanced at high polymerization temperatures and long reaction times.[11,25] Thus, the introduction of ε-CL in PLLA chain decreases the sequence length of L-LA-unit. Average values of 12, 6 and 4 repeated units of L-LA were found for the feeds with 10, 20 and 30 mol% of ε-CL respectively. The value of $\mathrm{I_{CL}}$ stays quite constant whatever the ε-CL molar ratio.

Thermal properties of the copolymers matrices were determined by DSC analysis. The melting temperature ($\mathrm{T_m}$), glass transition temperature ($\mathrm{T_g}$) and crystallinity ($\mathrm{X_c}$) are summarized in Table . DSC curves are presented in Figure 2. $\mathrm{T_m}$ and $\mathrm{X_c}$ were determined from the first scan, whereas $\mathrm{T_g}$ was determined from the second scan. As expected for statistical copolymers, a single glass transition temperature ($\mathrm{T_g}$) was observed for all samples, with values decreasing along with the increase of ε-CL content in the sample, from 54°C for pure PLLA matrix (run 1) down to 16°C for 30 mol% ε-CL content copolymer (run 6). Regarding the melting temperature and the crystallinities, they also both shift to lower values when increasing the ε-CL content in the copolymer, what is consistent with the decrease of the $\mathrm{I_{LA}}$ blocks, from 170°C for pure PLLA (run 1) down to 123°C for the copolymer with the highest content of ε-CL (run 6). Consequently, the crystallinity is thus impacted in the same manner, with 25 and 12 to 18 % for 10 and 20 mol% ε-CL respectively, whereas pure PLLA display a value superior to 60 % (run 1). The copolymer with 30 wt% ε-CL was found to be amorphous.

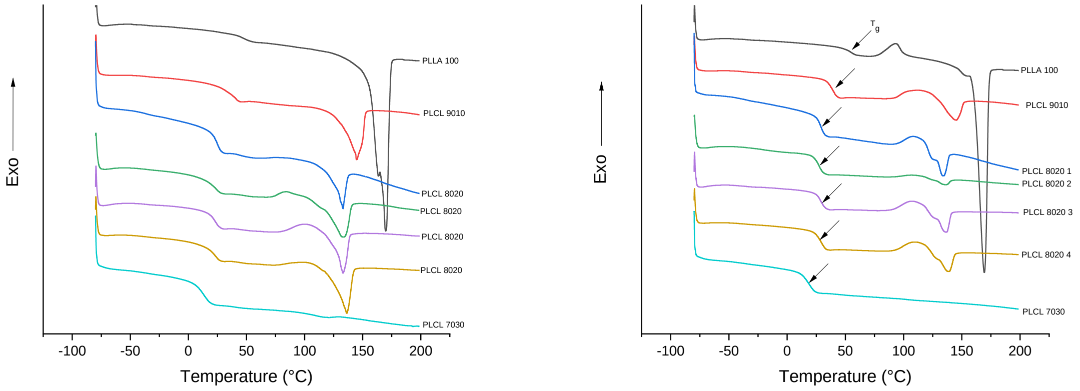

Figure 2: DSC thermograms of PLLA and copolymer matrices (left: first scan, right: second scan).

In addition, one can observe that for all composite specimens the filling of the mold cavity is efficient by observation of the resulting composites prototypes obtained (figure 3). Moreover, the optical microscopy analyses of the surface of sample from run 5 after being cross-cut shows a good impregnation of the fabrics by the matrix, as no lack of material nor voids are visible (figure 4)

Figure 3. Poly(L-Lactide-co-ε-caprolactone) / glass fabrics composite (20 wt% ε-CL, 120×120×50 mm, run 5)

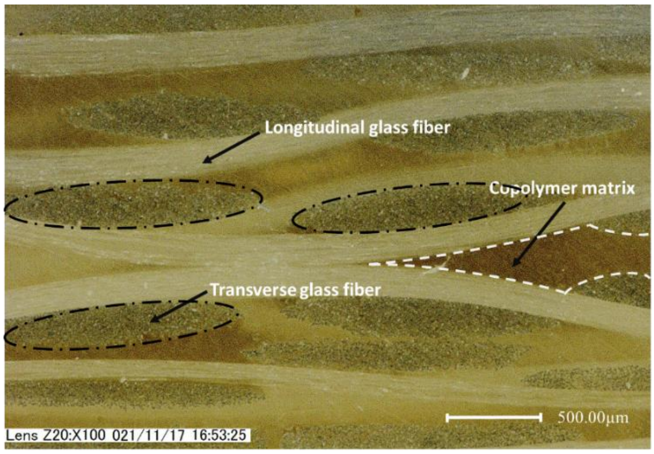

Figure 4. Optical microscopy picture of matrix composite with 20 mol% ε-CL (run 5)

In this contribution we reported the first prototypes of poly(L-lactide-co-ε-caprolactone) / glass fabrics composites. These unprecedented materials were produced by TP-RTM, a solvent-free single-step process. The copolymer matrices of the resulting composites display a random character along with molar masses as high as 71000 g.mol^{-1} and narrow dispersities. Optical microscopy analysis showed a good impregnation of the fabrics by the matrix, arising by from the process itself where the resin injected displays a low viscosity. In opposition to neat PLLA-composite which is highly rigid (Figure 5, top), the copolymer-based composite containing 30 mol% ε-CL displays a strong rubbery character (T_g = 16°C), highlighting the impact of the incorporation of ε-caprolactone in the macromolecular chain (Figure 5, down).

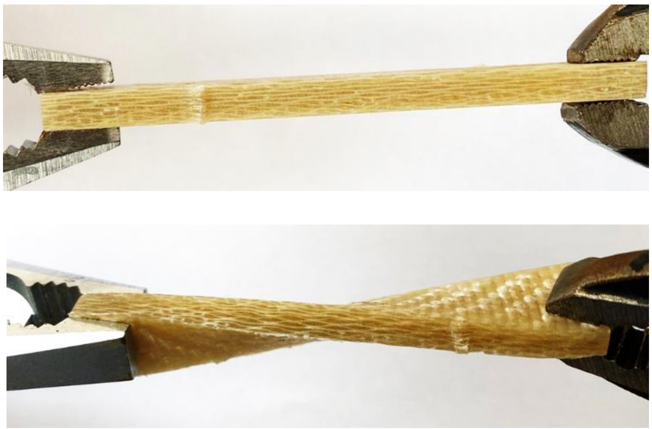

Figure 5. PLLA / glass fabric (run 1, top) and P(L-LA-co-CL) / glass fabrics (run 6, 30 mol% CL, down)

To assess the benefits of introducing ε-CL into PLLA on the mechanical properties of the material, Charpy impact tests have been carried out on the neat PLLA composite and the poly(L-lactide-co-ε-caprolactone) composite containing 30 wt% ε-CL. An increase of the absorbed energy of 178 % has been measured for the composite with 30 wt% ε-CL (Ea = 138 J/m^2 for neat PLLA composite *vs* 246 J/m^2 for the poly(L-lactide-co-ε-caprolactone) composite with 30 wt% ε-CL). This clearly shows that the addition of ε-CL has a high impact on the properties of such composites and seems to be a promising route to develop tough glass fiber reinforced thermoplastic composites.

These new PLLA-based / fabrics composites have never been reported to date by any other composite process, and constitute a brand new family of biobased materials. A deep mechanical characterization of these composite prototypes is in progress.

Table 1 : Preparation of Poly(L-Lactide) and poly(L-lactide-co-ε-caprolactone) / glass fabrics by TP-RTM [a]

Run	[L-LA]$_0$ / [CL]$_0$	[L-LA + ε-CL]$_0$ / [Sn]$_0$	Conversion [b] (%)		Copolymer Composition [b] (%)		Molar mass [c]			Average dyad relative molar fractions [d] (%)			Microstructural magnitudes of the copolymers [d]					Thermal properties [e]		
			L-LA	ε-CL	L-LA	ε-CL	M_n (g.mol^{-1})	M_w (g.mol^{-1})	$Đ$	(CL-CL)	(CL-LA)	(LA-LA)	I_{LA}	I_{CL}	$I_{LA\ (Random)}$	$I_{CL(Random)}$	R	T_m (°C)	T_g (°C)	X_c (%)
1	100 / 0	2000	97	-	100	0	87980	121200	1.37	-	-	-	-	-	-	-	-	170	54	62.3
2	90 / 10	2000	96	94	90.7	9.3	71100	90600	1.27	1.8	14.9	83.2	12.2	1.2	10.8	1.1	0.89	144	38	24.7
3	80 / 20	2000	97	96	79.7	20.3	43200	61340	1.42	7.3	25.9	66.8	6.2	1.6	4.9	1.3	0.80	133	29	13.1
4	80 / 20	3000	97	96	80.4	19.6	51600	68900	1.37	6.9	25.4	67.7	6.3	1.5	5.1	1.2	0.80	134	27	14.5
5	80 / 20	4000	97	89	79.5	20.5	52200	69000	1.32	7.8	25.3	66.9	6.3	1.6	4.9	1.3	0.84	139	30	25.4
6	70 / 30	2000	96	94	74.6	25.4	53230	71510	1.34	10.2	30,5	59.3	4.9	1.7	3.9	1.3	0.80	123	16	1.2

[a] Experimental conditions: T=185°C, 5h except run 1 2h, Sn(Oct)$_2$ as catalyst, m(L-LA + ε-CL) = 200 g, 10 layers of woven glass fabrics corresponding to 45-49 wt% in the final composite, mold dimensions = 120 mm x 120 mm. [b] Determined by ^{1}H NMR in CDCl$_3$. [c] Absolute M_n measured by SEC in CHCl$_3$ at 22°C with a triple detection system equipped with a multiangle light scattering and RI detectors.[d] The average dyad relative molar fractions and the microstructural magnitudes of the copolymers was calculated using the Bernoullian model for copolymer sequencing with the signals obtained by ^{1}H NMR spectroscopy (Bruker Avance 300 MHz) in CDCl$_3$. [e] Determined by DSC: T_m and X_c were determined at first scan and T_g at second one.

Acknowledgements

The authors would like to thanks Aurélie Malfait for SEC analysis and Johan Sarazin for TP-RTM mold design.

Funding sources

This worked was funded by the Region Hauts de France, the University of Lille and CNRS. The European Regional Development Fund (FEDER), Chevreul Institute (FR 2638), Ministère de l'Enseignement Supérieur de la Recherche et de l'Innovation, are also acknowledged for supporting and funding partially this work.

Supporting information

Experimental details, preliminary bulk copolymerizations experiments at small scale (Table S1), determination of the microstructure of the final copolymer matrices and SEC chromatograms are available in the SI.

References

[1] 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.

[2] Auras, R.; Lim, L-T.; Selke, S. E. M.; Tsuji, H. *Poly(Lactic Acid): Synthesis, Structures, Properties, Processing, And Applications*, 1st ed.; John Wiley & Sons : New Jersey, USA, **2010**; pp. 67-153.

[3] Hiljanen, M.; Varpomaa, P.; Seppälä, J.; Törmälä, P. Modification of poly(L-lactides) by blending: mechanical and hydrolytic behavior. *Macromol. Chem. Phys.* **1996**, *197*, 1503-1523.

[4] Krishnan, S.; Pandey, P.; Mohanty, S.; Nayak, S. K. Toughening of Polylactic Acid: An Overview of Research Progress. *Polym. - Plast. Technol. Eng.* **2016**, *55* (15), 1623-1652.

---

[5] Murariu, M.; Dubois, P. PLA Composites: From Production to Properties. *Adv. Drug Deliv. Rev.* **2016**, *107*, 17-46.

[6] Berl, M.; Kricheldorf, H. R.; Scharnagl, N. Polymerisation Mechanism of Metal Alkoxide Initiated Polymerisations of Lactide and Various Lactones. *Macromolecules* **1988**, *21* (12), 286-293.

[7] Kricheldof, H. R.; Kreiser-Saunders, I. Polvlactides - Synthesis. Characterization and Medical Application *Macromol Symp* **1996**, *103*, 85-102.

[8] De Castro, M. L.; Wang, S. H. Statistical Copolymers of l,l-Lactide and ε-Caprolactone. *Polym. Bull.* **2003**, *51* (2), 151–158.

[9] Stirling, E.; Champouret, Y.; Visseaux, M. Catalytic Metal-Based Systems for Controlled Statistical Copolymerisation of Lactide with a Lactone. *Polym. Chem.* **2018**, *9* (19), 2517–2531.

[10] Fernández, J.; Etxeberria, A.; Sarasua, J. R. Synthesis, Structure and Properties of Poly(L-Lactide-co-ε-Caprolactone) Statistical Copolymers. *J. Mech. Behav. Biomed. Mater.* **2012**, *9*, 100–112.

[11] Grijpma, D. W.; Pennings, A. J. Polymerization Temperature Effects on the Properties of L-Lactide and ε-Caprolactone Copolymers. *Polym. Bull.* **1991**, *25* (3), 335–341.

[12] Vazquez-Nunez, E.; Avecilla-Ramırez, A. M.; Vergara-Porras, B.; Del Rocıo Lopez-Cuellar, M. Green composites and their contribution toward sustainability: A review. *Polym. Polym. Compos.* **2021**, *29* (9) 1588–1608.

[13] Rudd, D. Resin transfer molding and structural reaction injection molding. In: ASM Handbook Volume 21 Composites, 1st ed.; Miracle, D.B.; Donaldson, S.L., ASM International: Ohio, USA, **2001**; pp. 492–500.

[14] Van Rijswijk, K.; Bersee, H. E. N. Reactive Processing of Textile Fiber-Reinforced Thermoplastic Composites - An Overview. *Compos. Part A Appl. Sci. Manuf.* **2007**, *38* (3), 666–681.

[15] Ageyeva, T.; Sibikin, I.; Kovács, J. G. A Review of Thermoplastic Resin Transfer Molding: Process Modeling and Simulation. *Polymers* (Basel). **2019**, *11*, 1555-1183.

---

[16] 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.

[17] Corden, T. J.; Jones, I. A.; Rudd, C. D.; Christian, P.; Downes, S. Initial Development into a Novel Technique for Manufacturing a Long Fibre Thermoplastic Bioabsorbable Composite: In-Situ Polymerisation of Poly-ε-Caprolactone. *Compos. Part A Appl. Sci. Manuf.* **1999**, *30* (6), 737–746.

[18] Christian, P.; Jones, I. A.; Rudd, C. D.; Campbell, R. I.; Corden, T. J. Monomer Transfer Moulding and Rapid Prototyping Methods for Fibre Reinforced Thermoplastics for Medical Applications. *Compos. - Part A Appl. Sci. Manuf.* **2001**, *32* (7), 969–976.

[19] Louisy, E.; Samyn, F.; Bourbigot, S.; Fontaine, G.; Bonnet, F. Preparation of Glass Fabric/Poly(L-Lactide) Composites by Thermoplastic Resin Transfer Molding. *Polymers (Basel).* **2019**, *11* (2), 339.

[20] Amirian, M.; Sui, J.; Chakoli, A. N.; Cai, W. Properties and Degradation Behavior of Surface Functionalized MWCNT/Poly(L-Lactide-Co-e-Caprolactone) Biodegradable Nanocomposites. *J. Appl. Polym. Sci.* **2010**, *122* (5), 3133–3144.

[21] Li, K.; Huang, J.; Gao, H.; Zhong, Y.; Cao, X.; Chen, Y.; Zhang, L.; Cai, J. Reinforced Mechanical Properties and Tunable Biodegradability in Nanoporous Cellulose Gels: Poly(l-Lactide-Co-Caprolactone) Nanocomposites. *Biomacromolecules* **2016**, *17* (4), 1506–1515.

[22] Tainio, J.; Paakinaho, K.; Ahola, N.; Hannula, M.; Hyttinen, J.; Kellomäki, M.; Massera, J. In Vitro Degradation of Borosilicate Bioactive Glass and Poly(L-Lactide-co-ε-Caprolactone) Composite Scaffolds. *Materials (Basel).* **2017**, *10* (11), 1–13.

[23] Jacobsen, S.; Fritz, H.G.; Degée, P.; Dubois, P.; Jérôme, R. Single-step reactive extrusion of PLLA in a corotating twin-screw extruder promoted by 2-ethylhexanoic acid tin(II) salt and triphenylphosphine **2000**, *41* (9), 3395-3403.

[24] Herbert, I. R. *NMR Spectroscopy of Polymers*, 1st ed.; Ibbet, R. N., Ed.; Chapman & Hall, **1993**.

---

[25] Kricheldorf, H. R.; Boettcher, C.; Tönnes, K. U. Polylactones: 23. Polymerization of Racemic and Meso d,l-Lactide with Various Organotin Catalysts-Stereochemical Aspects. *Polymer (Guildf).* **1992**, *33* (13), 2817–2824.