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ABSTRACT

Poly(lactic acid) (PLA) is a bio-based, bio-compostable and bio-compatible aliphatic polyester which derives from lactic acid. The interest for this bioplastic has increased in the last decade, as search for alternatives to oil-based plastics such as poly(ethylene) and poly(styrene), becoming compelling. PLA can be manufactured via two different routes: poly-condensation or ring-opening polymerization. The latter has been conducted successfully in combination with reactive extrusion (REX) to produce high molecular weight poly(L-lactide) (PLLA) with good mechanical properties. Reactive extrusion is a "green" process, which allows for continuous production without the use of toxic organic solvents. This technique can be paired with in situ chemical modification of PLA and compatibilization with other polymers. This includes the formation of copolymers, branched PLA and composites. The aim of this review is to provide an update on the last eight years of research dedicated to reactive extrusion applications on PLA.

Recent advances on reactive Extrusion of Poly(lactic acid)

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Introduction

Since the 50s, the production of plastics worldwide has skyrocketed to achieve 368 million tons in 2019 (Figure 1) but stagnated in 2020 due to the pandemic (1). A huge part of this plastics production is dedicated to short life applications, mainly in packaging industry (40.5 % in Europe) (1), with 150 million tons in 2015 (2). The other part concerns long-life applications such as electronic, transportation, building and construction. As the demand for plastics and their production is growing, the waste plastics production is also increasing and reached 300 million metric tons in 2015 (2). Moreover, a large majority of the plastics are arising for petroleum sources which are in a limited supply. This taken into account, and due to the environmental concerns, more and more academic and industrial studies are dedicated to the development of bioplastics.

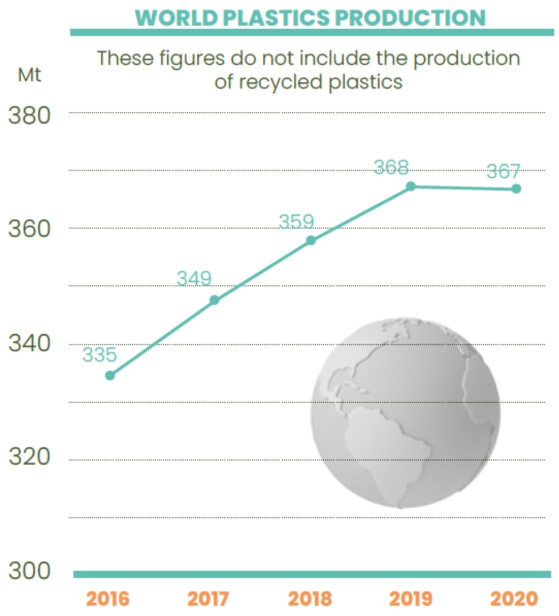


Figure 1 Global plastics production from 2016 to 2020 (1)

Although they only represent a minor part of the plastic production (circa 1 %), bioplastics are in a growing phase (3). Their use is still limited due to economic considerations, such as high production costs, and also inferior mechanical performances compared to usual fossil-based plastics (3). However, some biobased polyesters including poly(lactic acid) (PLA) and polybutylene succinate (PBS) have the potential to replace fossil-based polymers while fulfilling the requirements for circular economy, sustainability and properties (mechanical, processability and gas barrier performance) (3).

Among bioplastics, poly(lactic acid) also called polylactide is a bio-based, biocompatible and compostable thermoplastic polymer. It can be produced from renewable resources such as cellulose or starch (Figure 2) (3). PLA is synthesized either by direct polycondensation of lactic acid or by the ring-opening polymerization (ROP) of lactide (LA), a cyclic ester obtained by the di-cyclisation of lactic acid (Figure 2). Lactide monomer can be either L-lactide, D-lactide or *rac*-lactide (racemic mixture of L- and D-isomer) but L-lactide remains the most used as poly(L-lactide) (PLLA) is an isotactic semi-crystalline polymer which displays the best thermomechanical properties among polylactides. Therefore, as the present review focuses on PLLA exclusively, PLA will refer to PLLA all along the text. Regarding the polycondensation process, it requires a continuous removal of water under high pressure, high temperatures and long reaction time, leading to PLA with relatively low or medium molecular weights. On the other hand, the ROP process can be performed under milder experimental conditions, in solution or in bulk, giving rise to high molecular weight polymers in a few minutes without any by-products, making it faster, safer, and cheaper. Thus, ROP is the most current process involved in the industry for the production of PLA (4). The production of PLA by ROP can also be conducted by reactive extrusion (REX) (5,6), a process that requires the use of an extruder as a reactor where the polymerization reaction takes place in a continuous way.

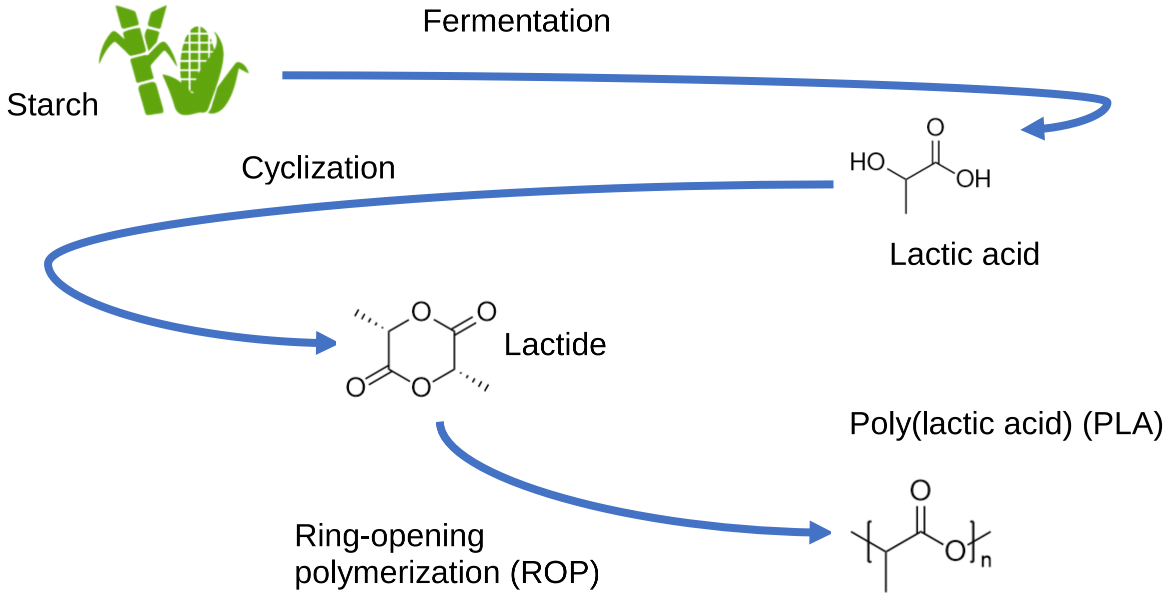


Figure 2 From starch to poly(lactic acid)

PLA displays properties similar to some petroleum-based polymers such as polystyrene (PS) and polyethylene terephthalate (PET) (7) in terms of mechanical strength and elastic recovery (8,9). Moreover, this thermoplastic polymer has a glossy optical appearance and displays good barrier properties toward water, oxygen and carbon dioxide (10). Thus, PLA can be used as an alternative to polyethylene (PE), polypropylene (PP), PS for short-life applications such as food packaging or single use cutlery (8,10). Moreover, its biocompatibility makes it an interesting material for medical applications such as suture, bone tissue engineering, skin regeneration or controlled release systems (10–13) in particular, poly(lactic-co-glycolic acid) is a copolymer that has been studied for its potential medical applications (11–13). PLA is also used in the textile industry to manufacture household and industrial wipes, diapers, feminine hygiene products, and disposable garments (9). However, its inferior thermal properties, heat distortion temperature, high flammability, and poor elongation at break limit its use (8,13). Commercial PLA often exhibits susceptibility to hydrolysis during processing and low crystallization rate (14). It also has to be noticed that within a few month at 58°C *i.e.* composting conditions, PLA degrades quickly (13).

Researches on improving PLA properties mainly focuses on blending PLA with other polymers or fillers to develop blends or composites. Commonly, the PLA blends with other polyesters are immiscible and necessitate the use of chemical compatibilizers. Some research also investigates a more challenging way to chemically modify PLA from lactide which can be done in many ways such as static mixing (15), autoclave (16) or reactive extrusion (6). However, in recent years, reactive extrusion is considered as the most economically viable and environmentally friendly modification technique in polymer processing (4).

This review will summarize the state of the art of the chemical modifications of PLA via reactive extrusion. This processing technique is the most used to modify PLA as its implementation is less challenging than the conventional chemical modification starting from lactide. The synthesis of PLA itself via reactive extrusion is also reviewed. This work will focus on the research developed after the publication of the book chapter *“Reactive Extrusion of PLA-based Materials: from Synthesis to Reactive Melt-blending”* (4)*.* Indeed, since 2014, the number of publications related to this topic has skyrocketed. Although there exist other reviews on the chemical modification of PLA using reactive extrusion, they primarily focused on more specific topics such as *e.g.* the foaming of chemically modified PLA (16) or the use of maleic anhydride functionalized PLA as a coupling agent (17). Therefore, a more general review on this topic is both relevant and timely.

I. Functionalization of PLA via reactive extrusion

As already mentioned, PLA displays good gas barrier properties as well as mechanical strength but also inherently low melt strength and other drawbacks. Thus, in order to enhance its properties various routes have been developed to perform PLA chemical modification such as radical-mediated chemical modification, blending PLA with other polymers or adding fillers to develop PLA-based composites.

1. Chemical modification of PLA

The most studied method to introduce branching in PLA is the use of peroxide initiators (18–27) that can introduce branching and cross-linking in the PLA macromolecules as well as promote the grafting of acrylate coagents (20–22). Some research on these coagents is based on the development of PLA “green” foams (14,16,28–33). In order to avoid the use of peroxide initiators, several researches are conducted on silanes (34–37), N-acetoxy-phthalimide (NAPI) (18,19), UV-irradiation (38,39) or epoxy-functionalized reagents (40–43).

1) Peroxide-mediated modification

PLA can be functionalized during the REX process with the help of peroxide initiators such as dicumyl peroxide (DCP) or benzoyl peroxide (BPO) (Figure 3). The macroradicals are formed by H-abstraction from the PLA backbone which allows the grafting of molecules onto PLA (18,19).

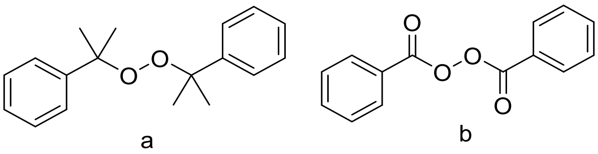


Figure 3 Chemical structure of dicumyl peroxide (DCP) (a) and benzoyl peroxide (BPO) (b)

Kontopoulou *et al.*(20–22) investigated the properties of branched PLA through different approaches. In a first study, the same branching strategy *i.e.* using triallyl trimesate (TAM) and DCP, was used to determine the structure-property relationship of branched PLA (20). The branching of PLA via peroxide-mediated REX provides a way to obtain PLA with enhanced crystallization kinetics and melt strength (20). Moreover, this process does not affect mechanical properties, nor the short-term decomposition profiles. Branched PLA displays high molecular weights resulting in an unnotched Izod impact strength twice higher than neat PLA (34 $kJ.m^{-2}$ vs 17 $kJ.m^{-2}$) (20). This study also demonstrated that various branched PLA can be designed by changing the amount of cross-linking agent. Therefore, branched PLA could be specifically designed to display properties that can meet the requirements of various industrial processes (20). Finally, a comparison was made between co-agent modified PLAs where peroxide-mediated REX was performed with allylic coagent (TAM) and acrylate coagents *i.e.* trimethylolpropane trimethacrylate (TMPTMA), trimethylolpropane triacrylate (TMPTA) and pentaerythritol triacrylate (PETA) (Figure 4) (21).

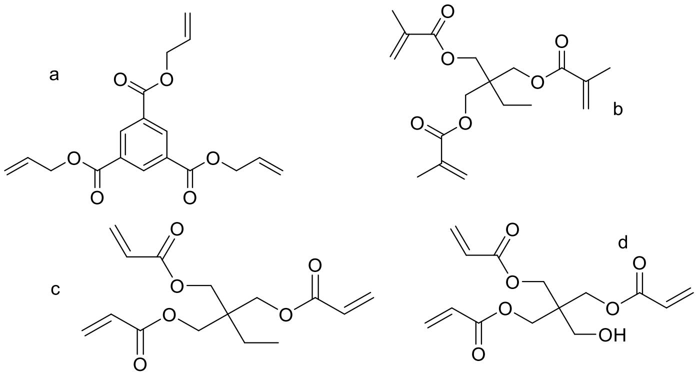


Figure 4 Chemical structure of used coagents: TAM (a), TMPTMA (b), TMPTA (c), PETA (d) (21)

Thus, the use of PETA as crosslinker led to low branch densities and a small increase of the activation energy for flow whereas TMPTMA was not able to increase the activation energy (21). Usually, the activation energy values are related to the branch density (21). Therefore, values around 75 kJ.mol^{-1} witness lower levels of branching (21). Moreover, due to the steric hindrance of its methyl groups and its tendency to homopolymerize, TMPTMA displayed poor grafting efficiency (21). TMPTA crosslinker was able to introduce branching but larger quantities were needed compared to TAM. Thus, the allylic coagent seems to be a better solution than the use of the acrylate-based crosslinkers. Long-chain branched PLA modified with TAM exhibited higher zero shear viscosity (2700 Pa.s), higher M_w (130 kg.mol^{-1}) and higher activation energy (112 kJ.mol^{-1}) resulting from a higher branching rate (21). Recently, the same group reported advances in peroxide-initiated graft modification (22). Coagents were used in combination with Joncryl ADR 4368 (a commercial chain-extender containing epoxy groups) to perform the chain extension of PLA. Among the tested coagents (TAM, PETA, TMPTA, TMPTMA and triallyl cyanurate (TAC)) TAM was found to be the most effective one (22) inducing higher branching degree with 25 % enhanced impact strength compared to neat PLA. The obtained PLA also displays 48 % crystallinity and has a lower crystallization half time of 0.6 min at 135°C instead of 9.3 min for PLA extended with Joncryl ADR 4368 (22).

Another work by Taha *et al.*(23) described the grafting of PLA and poly(3-hydroxybutyrate) (PHB) onto poly(methyl methacrylate) (PMMA). The grafting efficiency is influenced by the temperature, the catalyst and its concentration (23). Results showed that tin(II) octoate (Sn(Oct)2) gave rise to blends with the highest grafting degree compared to those obtained with 1,5,7-triazabicyclodec-5-ene (TBD) (Figure 5) (23). In another study, the grafting of itaconic anhydride (IA) onto PLA via REX was done using dicumyl peroxide (DCP) (10). PLA grafted IA displayed altered thermal properties indeed, the glass transition temperature (T_g) was reduced from 5 to 15 % depending on both IA and DCP contents. Moreover, the crystallinity of PLA increases depending on the degree of grafting (0-0.75 % determined by titration) (10). The grafted PLA obtained in the previous two cases (10,23) may be used as a compatibilizer in blends of PLA with another polymer such as acrylonitrile butadiene styrene (ABS) or polyamide (PA).

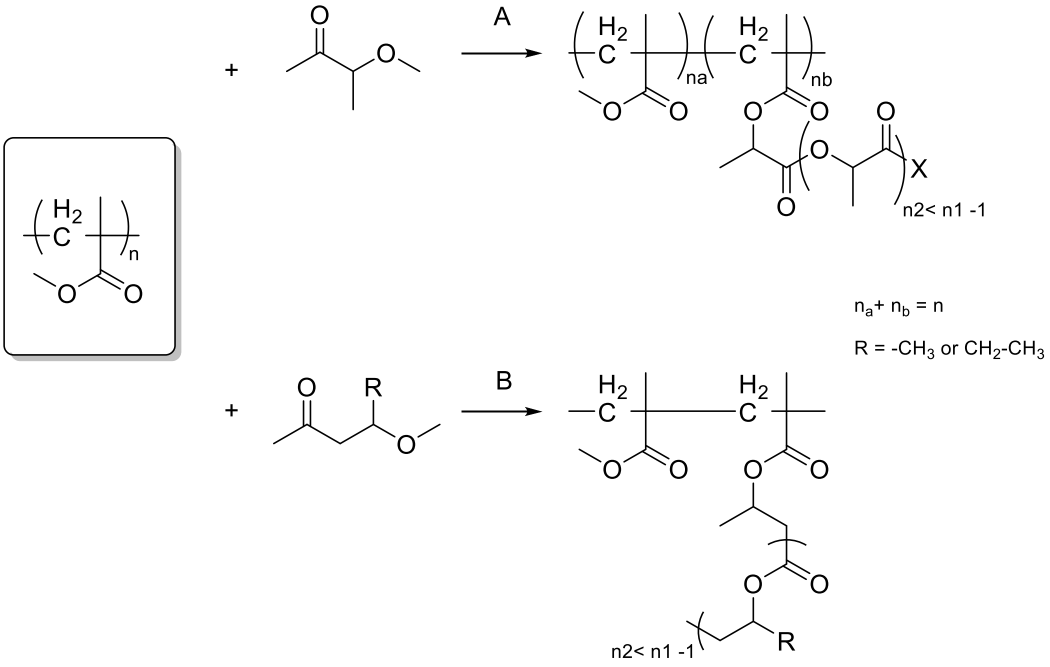


Figure 5 PMMA-g-PLA (A) and PMMA-g-PHB (B) syntheses by exchange reactions (23)

The peroxide-mediated grafting of PLA is also used to obtain long chain-branched (LCB) PLA (24,25). For example, metal-chelating nitrilotriacetic acid (NTA) ligands were grafted onto PLA via REX using DCP as peroxide initiator (Figure 6). This method was developed to produce non-migratory antioxidant PLA-based packaging. The obtained LBC PLA displayed hydrophobic properties *e.g.* a contact angle close to 90° as well as an ability to delay ascorbic acid decomposition which demonstrate its antioxidant properties.

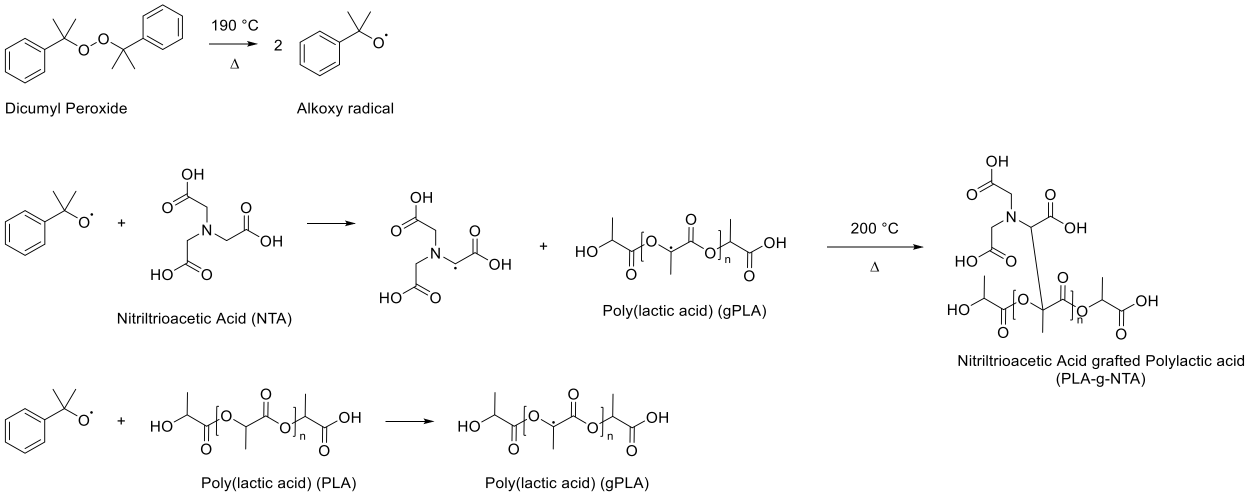


Figure 6 Grafting of NTA onto PLA via REX (24)

Khajeheian *et al.*(25) used the REX process to develop branched PLA in the presence of peroxides *e.g.* tertbutyl-peroxybenzoate (TBPB), 2,5-dimethyl-2,5-di-(tertbutylperoxy)-hexane, Lupersol 101 (L101) and BPO (25). In addition, itaconic anhydride was used as a chain-extender. Depending on the chosen peroxide and the REX conditions (190°C or 235°C), branched and partially cross-linked PLAs were obtained. Due to their enhanced thermal stability, they were proved to be able to withstand several heat treatments which make them re-meltable (25) and tend to suggest that they may be recyclable. The use of L101 to functionalize PLA was recently published by Tachaboonyakiat *et al.*(27) The aim was to graft polyethyleneimine (PEI) onto PLA via *in situ* REX in order to add functional groups along the polymer chain. Therefore, PLA was first modified with maleic anhydride (MAH) using L101 as initiator and then to types of PEI (PEI_{800} and PEI_{25k}) reacted by the ring opening reaction of both anhydride and amino groups (Figure 7) (27). DSC analysis gave insights on the thermal properties of the modified PLA indeed the addition of PEI lowered the T_g compared to neat PLA (56°C vs 58°C). Moreover, the PLA-PEI_{800} exhibited an enhanced crystallinity rate (24% vs 9%). The authors expect PLA-PEI_{800} to display enhanced mechanical properties compared to neat PLA; it should be assessed in another study. Another goal of this work was to study the biological properties of PLA-PEI_x since a few research assessed the antimicrobial activity of PEI and its use in coating for medical devices and drug carriers (27). Results showed that PLA-PEI displayed antibacterial activity against the representative Gram-positive bacterium *S. aureus*. Further research should be done to confirm these first results which may open a wider range of application for PLA in the medical field (27).

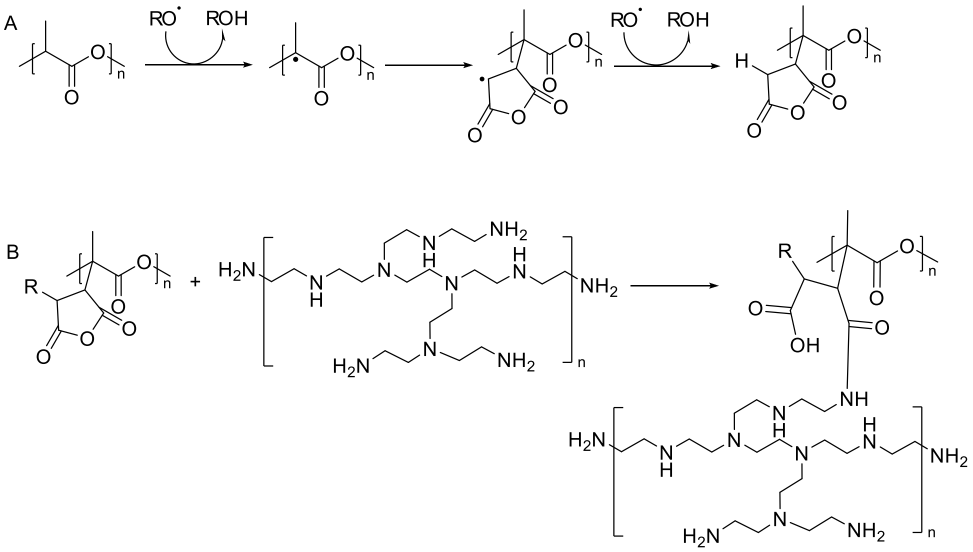


Figure 7 Grafting reaction of ***A*** *PLA with MA and* ***B*** *PLA-MA with PEI* (27)

Long chain-branched PLA may degrade differently than neat PLA. A study investigated the hydrolytic decomposition of LCB PLA with TAM and DCP as peroxide initiators (26). Mass loss and thermal properties of LCB PLA and neat PLA were evaluated during their exposition at 60°C in an environmental chamber with controlled pH using phosphate buffer solution (26). It turned out that the branching does not delay the hydrolytic decomposition of PLA (Figure 8) (26). However, the mass loss of the modified samples differs from the one of the unmodified PLA. Indeed, low and high molecular weight segments are preferentially degraded and the resulting oligomers have a counter-diffusion effect (26).

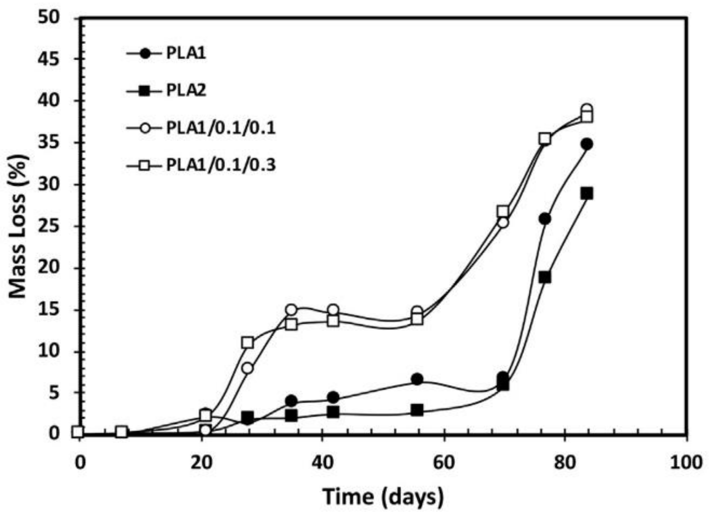


Figure 8 Mass loss as a function of hydrolysis time for low molecular weight unmodified PLA (PLA1), high molecular weight unmodified PLA (PLA2), low molecular weight PLA modified with 0.1 wt % DCP and 0.1 wt % TAM (PLA1/0.1/0.1) and with 0.1 wt % DCP and 0.3 wt % TAM (PLA1/0.1/0.3) (26)

Thus, LCB PLA may find applications in fields that require degradable biopolymers with enhanced mechanical properties. Indeed, the previous studies (20–26) showed that introducing branching in the PLA matrix provides a better impact strength but also higher thermal stability. Therefore, since its biodegradability is not hindered by the chemical modification, LCB PLA becomes an interesting material, especially in the medical field or for single-use cutlery. However, a limitation to these studies is the biocompatibility of the used coagents (TAM, PETA, TMPTA, TMPTMA). Indeed, the incorporation of chain extenders may hinder this property of PLA.

2) Peroxide-mediated modification of PLA for foaming

Industrial sectors including thermal and acoustic insulation, packaging and upholstery are interested in PLA as a green alternative to polymer foams (29). However, the foamability of PLA is poor due to its low melt strength but also due to its semi-rigid molecular structure that induces poor crystallization (28). Therefore, the following studies focus on the improvement of PLA foamability (14,16,28–33).

In 2017, a paper presented PLA functionalization via REX using DCP and a multi-functional co-agent triallyl-trimesate (TAM) to develop high density foams (29). The obtained PLA was then foamed using supercritical nitrogen. The results showed that the modified PLA displayed enhanced nucleation activity allowing the production of foams with higher cell densities (10^{11} cells/cm^3) and lower cell sizes than unmodified foamed PLA (29).

The aim of Kong *et al.*(30) study was to develop long-chain branched PLA that could meet the requirement of applications above 50°C. Thus, they investigated the use of low-content (0.3 wt %) cyclic organic peroxides (COP) initiators combined to acrylate coagents *i.e.* 1,4-butanediol diacrylate (BDDA), trimethylolpropane triacrylate (TMPTA) and pentaerythritol tetraacrylate (PETA). The results showed that the addition of coagents prevents the formation of byproducts and led to LCB-PLA with enhanced branching degree (30). The heat resistance assessment of the obtained LCB-PLA highlighted an increased crystallinity (24 % *vs* 8 % for neat PLA) leading to an improved heat resistance *e.g.* the Vicat softening temperature increased up to 153°C whereas it is only 60°C for neat PLA. Since its melt strength and crystallinity were improved, LCB-PLA also displayed improved foaming properties. Indeed, polymers with high extensional viscosity and high melt extensivity as well as high melt strength are required for foaming (33).

Another study used soybean oil (SO) to introduce long-chain branching into PLA (28). Indeed, SO has the advantage to be renewable, biodegradable and non-toxic, thus, the obtained long-chain branched PLA keeps its biodegradability. The branching reaction was initiated by low amount of cyclic peroxide during a REX process. LCB-PLA was foamed via extrusion foaming using supercritical carbon dioxide (28).

The foaming properties of chemically modified PLA using REX were also studied by Göttermann *et al*.(31) Tris(2,3-epoxypropyl) isocyanurate (TGIC), hexamethylene diisocyanate (HDI), 1,3-Phenylene-bis-oxazoline (PBO), styrene maleic anhydride (SMA) copolymer, organic peroxide (DCUP), were used as different chain extenders and dicumyl peroxide as the peroxide initiator. The highest molecular weight of 237.600 g.mol^{-1} was reached using dicumyl peroxide at 0.2 % weight concentration, *vs.* 130,000 g.mol^{-1} for unmodified PLA. This resulted in better results than those obtained with Joncryl (multifunctional epoxy) (31). All the reactive blends (except the one modified with TGIC and HDI) display a lower crystallinity compared to neat PLA (25 %). Modification of the backbone hinders the packing of the chains. The lower the crystallinity, the larger the modifier chains and the more PLA chains are hindered in their crystallization. The best thermal or crystallization properties were observed for the DCUP modified PLA (PLA2) even if its crystallinity is just slightly lower than in the neat PLA (20 % compared to 25 %). It is also the only blend that crystallizes during the cooling process. This phenomenon is due to a higher crystallization speed resulting from the branched chains that have a nucleating effect. This leads to a significantly higher melt strength, which is fundamental for extrusion foaming, as it allows the building of a stable foam structure by reducing cell collapse (31).

Magaraphan et al.(32) reported the use of ethoxylated bisphenol A dimethacrylates (Bis-EMA), which have a rigid difunctional structure and exhibit low water absorption, as a cross-linking agent (32). When introduced with DCP in the PLA matrix, it induces cross-linking of the obtained polymer resulting in the improvement of the storage modulus (up to 3500 MPa at 30°C vs 1900 MPa for neat PLA) and the complex viscosity of PLA. Unfortunately, thermal properties decrease while increasing the amount of Bis-EMA. Indeed, the maximum decomposition temperature ranges from

389°C for PLA with 0.3 % of DCP to 385°C for PLA with 0.1 % of DCP and 7 % of Bis-EMA (32).

In others studies, Altstädt et *al.*(14,16,33) investigated the influence of chain extension onto foamed PLA. In a first study, chain extended PLA was prepared with five different chain extenders (CE) (multifunctional epoxide (PLA_1), organic peroxide (PLA_2), styrene maleic anhydride (PLA_3), bis-oxazoline and diisocyanate (PLA_4), isocyranurate and diisocyanate (PLA_5)) using DCP as peroxide initiator (16). The obtained PLAs were then foamed in autoclave (Figure 9). The use of multifunctional epoxide CE or organic peroxide CE led to the highest molecular weights. In particular, organic peroxide allowed the formation of larger cells while foaming due to a high elongation viscosity of the branched polymer. However, the rheological study revealed a viscosity reduction for all modified PLAs due to the onset of degradation after 15 min (16). In a more recent study, the results highlighted the influence of the molecular weight and D-lactide content in commercial PLA. This D-lactide content is usually low *i.e.* from 0.5 to 4% but some commercial PLA can reach 12% of D-lactide content. A suitable foaming of PLA requires, a slow and low crystallization and is dependent of the D-lactide content, the melt strength and the zero complex viscosity of PLA (14). Moreover, the rheological study in the presence of carbon dioxide (CO_2) showed an inhibition of the CE as well as a higher gas diffusion. These parameters need to be taken into account to perform the reactive foam extrusion of the branched PLA (33).

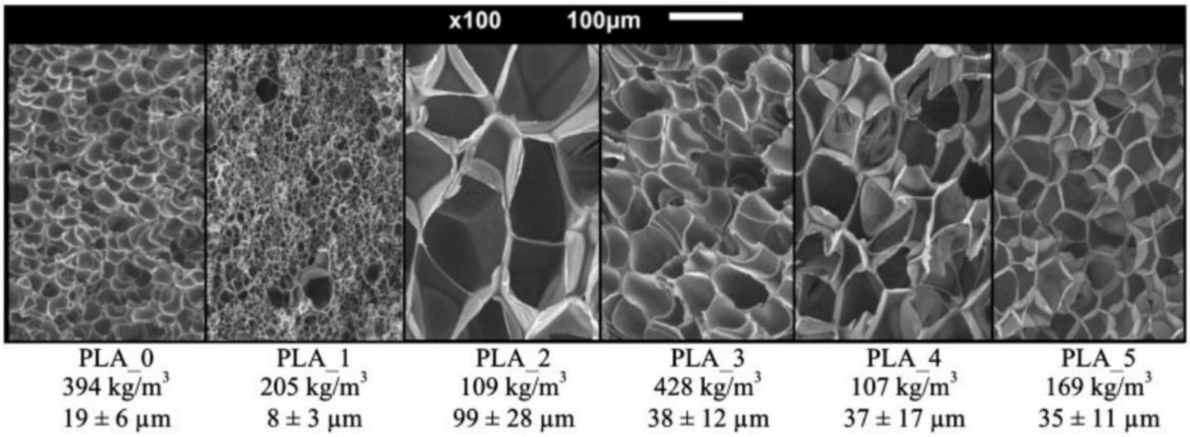


Figure 9 SEM images, foam density and cell sizes of neat and modified PLA samples (16)

The previous studies aim to enhance the foamability of PLA in order to develop bio-based foams that will find a use as insulation materials. However, even though the foamability of PLA is assessed, its insulation capacity should be studied as well with a comparison between PLA foam and usual insulation foams.

3) Alternatives to peroxide initiated modification

Silane mediated modification

The crosslinking of PLA with the help of silane is energy saving (34) compared to usual techniques such as peroxides or high energy radiation initiation. Moreover, it displayed higher productivity and the hybrid polymers contain stable siloxane (Si–O–Si) bonds.(34)

Through a free-radical grafting reaction that creates both grafting and cross-linking, Narayan *et al.*(34) produced PLA-grafted vinyltrimethoxysilane (VTMOS). The grafting results from the vinyl function of VTMOS while crosslinks are formed through moisture curing thanks to the alkoxysilane group (Figure 10).(34) The addition of silanol-terminated poly(dimethylsiloxane) allowed the formation of longer siloxane crosslinks (Figure 10). It results in an enhancement of the tensile toughness as well as other mechanical properties *e.g.* elongation at break and impact toughness (28 J.m^{-1} vs 22 J.m^{-1} for neat PLA). SEM analysis pointed out that the siloxane crosslinks improved the ability of the hybrid PLA to deform and absorb energy leading to the enhanced toughness.(34) Indeed this technique allows the study of the sample morphology. Therefore, the fractured surfaces of samples that went through tensile and impact testing were analyzed. The SEM pictures showed the presence of white strands corresponding to the siloxane linkage.(34)

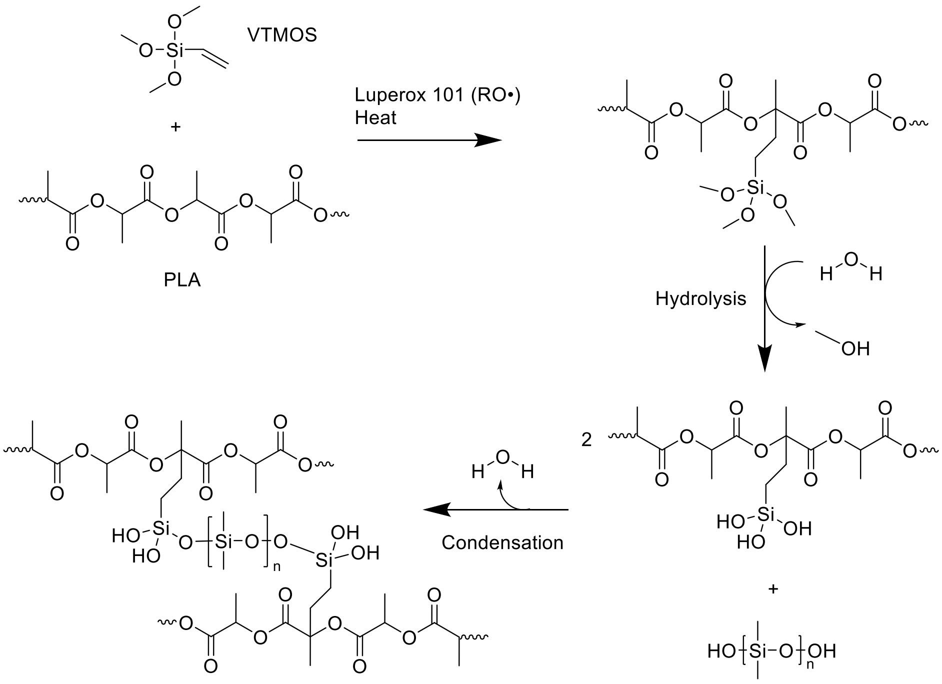


Figure 10 Schematic mechanism for the free radical initiated grafting of VTMOS on PLA and mechanism showing the hydrolysis of the methoxy groups and the condensation resulting in siloxane crosslinked PLA (34)

Ha *et al*.(35,36) prepared hybrid PLA via REX using functionalized silica. In a first study, epoxide-functionalized alkoxysilanes (GTMS) were grafted onto PLA through a chemical reaction between the cyclic epoxide groups and the nucleophilic end groups of PLA (Figure 11). The results of the mechanical tests highlighted the improved toughness of the hybrid PLA. Especially the complex viscosity of the modified polymer was increased probably as a result of enhanced topological interactions induced by GTMS.(35) Moreover, differential scanning calorimetry (DSC) thermograms showed that the crystalline fraction of the hybrid PLA was doubled in the presence of GTMS (39 % vs 18 %).(35)

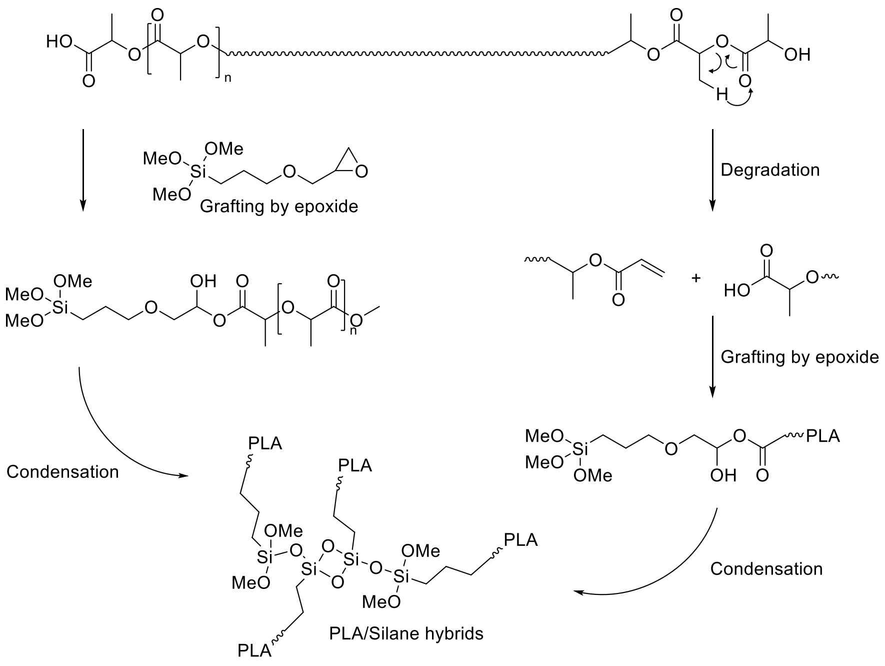


Figure 11 Mechanisms of PLA decomposition and grafting condensation reaction between PLA and GTMS(35)

In a second study, tetraethoxysilane (TEOS) was used with a fixed amount of GTMS to functionalize PLA (36). High molecular weights (M_n = 130 000 g.mol^{-1}) hybrid PLA were obtained and displayed crystallinity rates up to 57 % depending on the amount of TEOS (36). Mechanical properties of the hybrid polymer were positively affected as well as its thermal properties (36). Indeed, the maximum decomposition temperature of PLA hybrids reached 370°C which is slightly better than neat PLA (355°C). Moreover, the storage modulus of the hybrids was increased up to 200 MPa at low angular frequencies *vs* 80 MPa for neat PLA (36).

Alkoxy-modified silanes (phenyltriethoxysilane ($Ph-Si(OEt)_3$) and *N*-octyltriethoxysilane ($Oct-Si(OEt)_3$)) were studied to enhance PLA thermal properties as well as its hydrophobicity (37). The contact angle of LCB-PLA was increased (82° *vs* 69°) indicating better water resistance achieved with the incorporation of $Oct-Si(OEt)_3$. Moreover, the best results for mechanical properties were obtained by using 1.3 % of silane chain-extender *i.e.* $Oct-Si(OEt)_3$. With these conditions, the elongation at break of LCB-PLA was about 30 %, its tensile strength reached 240 MPa and achieved a Young's modulus close to 5 GPa.(37) However for sample with $Ph-Si(OEt)_3$, except for the Young's modulus, the same parameters were found to be lower *e.g.* the tensile strength dropped to 177 MPa and the elongation at break was only of 23 % (37). Finally, the TGA analysis shows that the addition of both silane chain-extenders does not hinder PLA thermal properties (37).

NAPI initiated modification

The grafting of PLA with maleic anhydride or itaconic anhydride (10) have been reported in the literature. It is usually initiated by conventional peroxides *e.g.* dicumyl peroxide (DCP) or benzoyl peroxide (BPO) that has the drawback to induce side reactions such as PLA chain scission, branching or cross-linking (18). Monge *et al.*(18,19) investigated the use of N-acetoxy-phthalimide (NAPI) as an alternative initiator to the usual peroxides for grafting of PLA via REX. Under heating, NAPI breaks down into nitroxide radicals that combine with the macroradicals of PLA and led to a better control of PLA structure while avoiding the side reactions (18,19). Moreover, the obtained grafting rates were similar to those obtained with the use of peroxides (0.4 mol %). However, the optimal concentration of NAPI was proven to be 50 times higher than the one of the reference peroxide initiator (Luperox 101) (19) under similar experimental condition, *i.e.* 200°C (2.5 mol % *vs* 0.05 mol %) (19). Therefore, the needed amount of NAPI could be questionable. Indeed, peroxide initiated modification requires smaller amount of peroxide initiator.

UV-induced modification

To avoid the use of peroxide initiator, Liao *et al.*(38) developed an ultraviolet-induced REX process that allowed a better control on the side reactions e.g. chain scission and branching reactions of PLA. A long-chain branched (LCB) PLA was obtained thanks to the addition of trimethylolpropane triacrylate (TMPTA) into the PLA matrix during the REX process (38). The LCB structure displays nucleating effect resulting in higher crystallization rates for LCB PLA compared to neat PLA (38) which may extend the application field of PLA. Moreover, the obtained LCB polymers are free from peroxides residues. Li *et al.*(39) studied the foaming using supercritical CO_2 of LCB-PLA prepared with the above mentioned protocol. The effect of the long-chain branching structure on the cell morphologies of PLA foams was investigated. The stronger matrix strength and higher nucleation potential of LCB-PLA turned out to be the main reason of its better foaming behavior (39).

Epoxy functionalized coagents

The development of chain-extension strategies of PLA may be a solution to overcome PLA tendency to degrade after reprocessing and make it recyclable (40). PLA was modified with a micro lamellar talc as mineral filler, Joncryl ADR 4368 as chain extender (CE) and an aliphatic polyester derived from succinic acid which was supposed to increase the flexibility of the PLA-based blend (40). Chain-extended PLA was then subjected to successive compounding processes. Characterizations of the obtained polymers were performed to assess their rheological, thermal and mechanical properties (40). Results showed that the addition of CE contributed to increase the elongation at break (up to 350 %), to restore partially the molecular weight when reprocessing (40). However, the process need to be improved in order to develop completely recyclable PLA.

Tzetzis *et al.*(44) also investigated the use of an epoxy chain extender (Joncryl ADR 4400) and studied its influence on 3D printed PLA. Joncryl-modified PLA exhibited enhanced melt flow index (0.37 *vs* 4.29 g/10 min) and complex viscosity (4000 *vs* 2500 Pa.s). The chain extension also allowed the increase of the molecular weight from 75,000 up to 125,000 g/mol. Moreover, mechanical tests revealed that the addition of 2 wt% of Joncryl afforded better performances to the modified PLA (44). Indeed, the elastic modulus was increased by almost 400 MPa (3945 *vs* 3572 MPa) and the hardness went from 142 MPa up to 157 MPa. The chain extension of PLA using Joncryl allowed this research group to print the obtained polymer using the fused deposition modelling process (44).

A one-step REX-calendering process was designed by Carrasco *et al.*(41) Their goal was to modify linear PDLLA using a styrene-acrylic multifunctional epoxide oligomeric agent (SAmfE) as reactive agent. The physical ageing and the properties of the obtained LCB-PLA was impacted by the long-chain branching induced by SAmfE. Indeed, the aged samples displayed a slightly enhanced strain at break (2.5 % *vs* 2.2%). The same group also investigated the optimization of the REX parameters and developed an analytical equation. It was designed for the modelling of the kinetic parameters related to the thermal decomposition of branched PLA (42).

Quiles-Carrillo *et al.*(43) prepared various blends of PLA / acrylated epoxidized soybean oil (AESO) using REX. The content of AESO (Figure 12) in the blends varied from 2.5 up to 10 %, with 2.5 % increments. After melt compounding, the formulations were injection molded. A slight decrease of tensile strength was observed for specimen with higher load of AESO (the highest decrease was observed for 10 % AESO content having a tensile strength below 60 MPa). However, the elongation at break of modified PLA reached a maximum for the blend containing 10 % AESO (*ie* 10.6 % increase) (43).

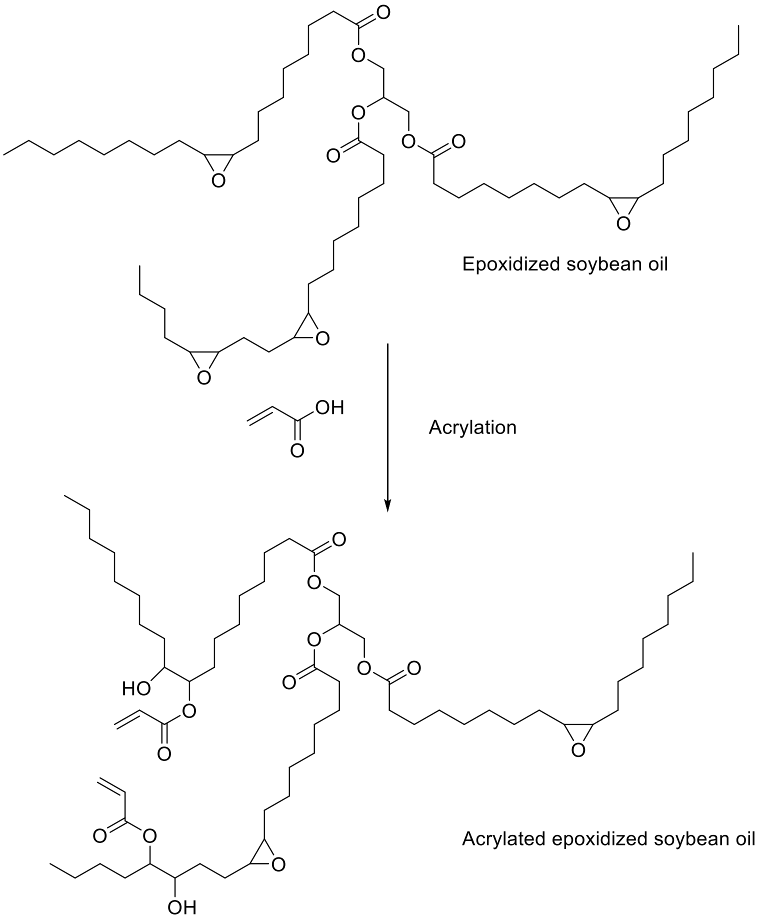


Figure 12 Schematic representation of the chemical structure of acrylated epoxidized soybean oil (AESO) obtained by acrylation of epoxidized soybean oil (ESO) with acrylic acid (AA) (43)

2. Blend Compatibilization

Reactive and unreactive blending of PLA with other polymer can be an interesting technique in terms of cost, scalability and environmental friendliness (45,46). Using different strategies such as plasticization, rubber toughening, or dynamic vulcanization, PLA with improved properties can be achieved. It can be blended with various oil-based polymers (acrylonitrile-butadiene-styrene (ABS) (46–52), polyamide (PA) (53,54), polyethylene (PE) (55,56)) however it often displays a limited compatibility with them. Therefore, different compatibilization strategies were studied *e.g.* the incorporation of epoxy agents (53), the use of functionalized soybean oil (43,57) or the addition of cardanol (46,51).

1) PLA / ABS Compatibilization

When PLA is blended with ABS the interfacial interaction is poor, leading to lower mechanical properties than neat PLA (47). In order to increase the bio-based content in ABS, the latter was blended with PLA (50 / 50 ratio) (48). Both an acrylic copolymer (Biostrenght 9000) and Joncryl chain extenders (ADR-4368C with epoxy functionality) were used to improve the interfacial adhesion between ABS and PLA. The blend containing the acrylic copolymer displays an elongation at break increased up to 140 % (*vs* 5 % for neat PLA and unmodified PLA / ABS blend) (48). The blend containing also Joncryl displayed a lower value while impact strength was increased to 250 J/m.(48) In another study, the same group used statistical analysis in order to find the best loadings of each component to improve the mechanical properties. The optimized blend contains 3.6 wt % of acrylic copolymer and 1.2 wt % of chain extender. This led to an increase of the impact strength by over 600 %, the elongation at break by over 1000 %, the tensile strength increased by 11 %, while the tensile modulus was increased by over 7 % (49).

Carrasco *et al.*(47) produced a PLA / ABS (70 / 30) blend compatibilized by adding styrene-acrylic multi-functional epoxide oligomeric agent (SAmfE). Initially PLA was reacted with SAmfE while ABS was processed with maleic anhydride (MAH). This enables the reaction of the hydroxyl and acid functions of the modified polymers and allows chain extension. Thermal decomposition analysis of the blends showed that temperature decomposition for PLA-REX, ABS and the blend were 335°C, 386°C and 303 °C, respectively (47). The same group, in a later study, assessed the decomposition kinetics during polymer processing (50). They compared PLA / ABS and PLA / ABS-g-MAH blends produced via reactive extrusion *i.e.* PLA−REX / ABS (70 / 30) to PLA−REX / ABS / ABS−g−MAH (70 / 24 / 6).(50) The decomposition temperature was increased by 90°C (from 463°C to 553°C) (50) when the compatibilizer was added.

In an another work conducted by Verge *et al.*(46) the compatibility of PLA / ABS blend was improved by the addition of cardanol (Figure 13), a bio-based phenolic compound, during the REX process. The authors proved that cardanol is able to react with the polybutadiene segments of ABS via radical pathway. Contrary to what was believed, cardanol grafting occurs on the aromatic ring thanks to the phenolic moiety and does not involve the double bonds of the alkyl chain (46). This group also studied the use of two different epoxidized cardanol monomers *i.e.* CardE and Ecard (Figure 13) to compatibilize the blend of PLA / ABS. CardE was produced by epoxidizing the double bounds while Ecard was obtained by reaction of epichlorohydrin at the phenolic hydroxyl group. Initially, studies were conducted to assess the reactivity of the two different compounds.

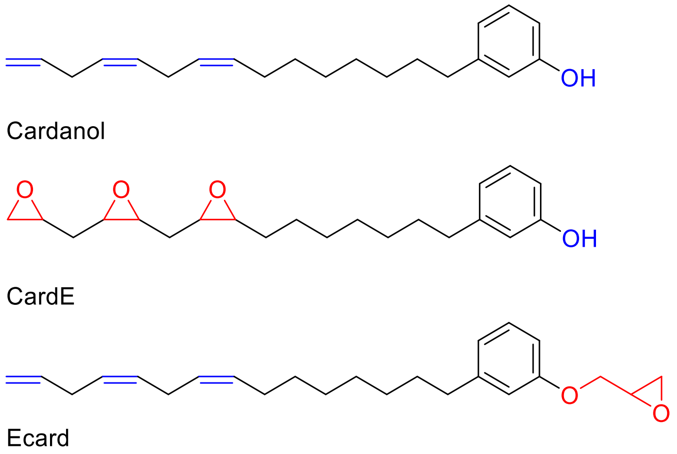


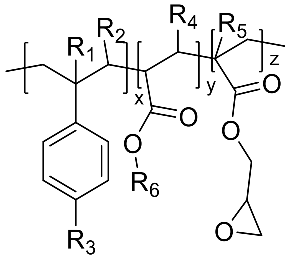
Figure 13 Cardanol and functionalized cardanol monomers (51)

These two compounds interact differently with ABS and PLA. PLA / CardE (5 wt %) and ABS / CardE (5 wt %) blends were prepared by extrusion in order to elucidate the mechanism of grafting. For the blend of PLA / CardE no reaction between the carboxylic end groups of PLA and the oxirane ring was observed (51). In turn, this does not result in a simultaneous reaction of the three components. CardE promotes the dispersion of ABS within PLA, however, at content above 5 % neat cardanol had detrimental effect. Trials were also conducted using a mixture of Ecard and cardanol which can both react with PLA and ABS (51). Results shown that with 10 wt. % of a 50 / 50 mixture, the PLA / ABS blends displayed and elongation at break up to 82.9 % and an impact resistance of 7.9 kJ.m^{-2} (51).

The blending of PLA and ABS using maleic-anhydride-modified ABS as the compatibilizer was studied by Abt *et al*.(52) These blends were prepared in three different steps. Modified PLA was first prepared by adding 0.6 wt % of Joncryl via a reactive extrusion process. Then, this PLA was pelletized and mixed with or without ABS / ABS-g-MAH in various proportions (70 / 30 / 0, 70 / 27 / 3 and 70 / 24 / 6). The blends were then extruded, pelletized and injection molded. ABS dispersed in the PLA matrix forms rod-like dispersed morphology which led to a 30 % increase in the energy absorbed up to rupture compared to neat PLA (52).

2) PLA / PA Compatibilization

PLA / PA11 (polyamide 11) blends were prepared using reactive extrusion (53). These two polymers being immiscible, compatibilization is necessary and was done using Joncryl epoxide (Figure 14) (53). The blends PLA / PA11 (80 / 20 weight %) were elaborate with different amounts of Joncryl. This was conducted by firstly reacting PLA with 4 wt. % Joncryl. Modified PLA was then blended with PLA / PA11 giving blends with 0-3 wt. % of Joncryl. A reduction in PA11 dispersed phases diameter was observed, indicating compatibilization through coalescence suppression. Elongation at break was improved by 3.4 % for blends containing 2-3 % of Joncryl (53).



R_1–R_5 = H, CH_3, higher alkyl or combinations
R_6 = alkyl
$1 < x, y, z < 10$

Figure 14 Joncryl structure(53)

The work of Maazouz *et al*.(54) focused on improving the processability of PLA by reactive extrusion with PA11 with a chain extender (Joncryl ADR®-4368). Two different approaches were used: (i) all the components were added in the micro compounder at the same time or (ii) PLA and the chain extender are pre-mixed in the micro compounder prior to the addition of PA11 (54). Also, different ratios (100 / 0, 80 / 20, 60 / 40, 40 / 60, 20 / 80 and 0 / 100) (54) of PLA / PA11 were blended. For the one-step process, the SEM images show a reduction in particle size of the dispersed phase, compared to the blends without Joncryl. However, for the blends obtained in two steps process, there is a better adhesion between the polymer and the dispersed phases resulting in a reduced interfacial tension (1.37 *vs.* 2.57 mN/m for uncompatibilized blend) (54). It was shown that the incorporation of Joncryl in the blend allows a significant improvement of mechanical properties (viz. the elongation at break) increases from 20 % for the PLA / PA11 (80 / 20) blend to 260 % for the PLA / PA11 / Joncryl (80 / 20 / 0.7), however for the pre-modified PLA, the blend PLA-Joncryl /PA11 (80 / 0.7 / 20) showed an increase of 355 %. This was explained by the reaction of the two polymers with the chain extenders allowing better compatibilization of the two phases (54).

3) PLA / PHBV / PBAT compatibilization

Quiles-Carrillo *et al.* used reactive extrusion to produce ternary blends of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), PLA, and polybutylene adipate terephthalate (PBAT) (57). These blends were made miscible by adding an epoxy-based styrene–acrylic oligomer (ESAO, Joncryl) which react during melt compounding. Each individual polymer was premixed with Joncryl and then fed in the extruder, subsequently films were made using a press. Different blends were produced with various quantities of each component. The scanning electron microscope (SEM) images, show that for the neat biopolymers blend, small droplets were present in each phase indicating the thermodynamical immiscibility of the polymers. With the addition of Joncryl these phases are still present, however they are reduced in size (600 nm *vs* in the range of 2-10 µm without ESAO) indicating a better interfacial adhesion. This enhancement is rationalized by the formation of a block copolymer and terpolymer of PHBV-*b*-PLA-*b*-PBAT.(57) After the addition of low-functionality ESAO to the PHBV / PLA / PBAT 1:1:1 blend, the E (elastic modulus) and σ_y (tensile strength at yield) values were improved by more than 10 % and 35 %, respectively, while ε_b value was almost 8 times higher. Blends containing the highest amount of PHBV could be used as compostable food packaging. Indeed, they display similar properties to oil-based polymers such as PET, PS and polycarbonate (PC) *i.e.* PLA and PHBV can produce rigid films with an E about 800-1200 MPa and a σ_y about 30-40 MPa (57).

4) PLA / PE compatibilization

The production of PLA / PE block copolymers by REX using two different reaction pathways was investigated (55). Compatibilizer C1, was prepared by reacting oligomers of PLA with PE-*g*-MAH (polyethylene grafted maleic anhydride). Compatibilizer C2 involves the preparation of polyethylene containing a carboxylic moiety (PE-OH) obtained by polymerizing of ethylene with 10-undecenoic acid. Then, this pre-polymer was reacted with L-lactide via ROP using tin octoate as the catalyst.

This route is further developed in the ROP section. Compatibilizer C3 resulted of the polycondensation reaction of L-lactide with PE-g-MAH. All three synthesized compatibilizers were compared to a commercial one (C0) which was PE-g-MAH (Fusabond E226). The blends were then prepared via REX varying the amount of components: compatibilizer, PLA and HDPE (55). By TGA analysis, a two steps curve is observed witnessing the immiscibility of the two polymers (Figure 15). This statement is confirmed by the DSC results (Figure 15). Indeed, the compatibilized blend show a thermogram close to the one of PLA whereas uncompatibilized blends displays a 10°C lower cold crystallization exotherm (T_{cc}). Moreover, it can be noticed that C2 compatibilizer induces a significant shift of the melt endotherm of PLA / C2 / HDPE_A blend compared to all the other blends. According to the authors, this change is due to the synthetic pathway of C2 compatibilizer which created a different linkage between PLA and HDPE. The TGA analysis also show that the decomposition of each component catalyzes the decomposition of the other. This could be an advantage for the waste disposal, as a higher degradation rate is observed when the compatiblizer is present. Regarding the mechanical properties of the PLA / HDPE (80 / 15) blend, the one containing C2 compatibilizer displayed an elongation at beak of 7 % which represents a 5 % improvement compared to the uncompatibilized blend (55).

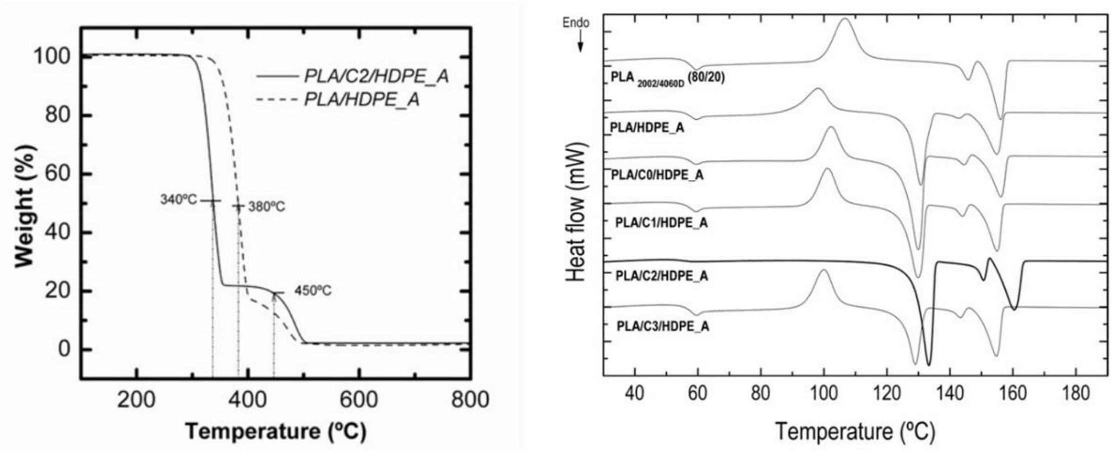


Figure 15 TGA analysis of PLA/HDPE_A and PLA/C2/HDPE and DSC thermograms of PLA, HDPE and different blends (55)

Bäckström *et al.*(56) developed a plasticizer, derived from oxidation of HDPE, composed of succinic / glutaric and adipic acid. This mixture was obtained by a microwave-assisted hydrothermal process; this involves oxidation of HDPE in a solution of a nitric acid with microwave heating. The resulting mixture contains succinic

/ glutaric / adipic acid in 0.49 / 0.39 / 0.12 ratio. To the acid mixture, 1,4-butanediol is added and polymerization is initiated by heating to 190 °C in order to produce the oligo-ester plasticizer. Then crotonic acid was subsequently added as end-capping group with a molar ratio of plasticizer/crotonic acid of 1/2. The blends were produced by pre-mixing 20 % of the 'recycled plasticizer' with PLA and solution casted. Afterwards, 0.19 mm thickness films were formed using a hot press. Then, Luperox101 (0.5 % weight) was added to the films and the resulting products were subsequently fed in the extruder. For the grafted blend the strain at break was increased from 6 % for PLA to 156 %, which corresponds to an increase of 26 times (56).

5) PLA / PGSMA compatibilization

The elongation at break of PLA was increased by blending with various formulations of poly(glycerol succinate) (PGS) and poly(glycerol succinate co maleate) (PGSMA). (45,58) PGSMA was synthesized using different ratios of glycerol, succinic acid and maleic anhydride.(58) Different parameters such as monomers molar ratio, reaction temperature and time, were varied to obtain a PGS gel and different end-chain moieties. Firstly, PLA / PGS (80 / 20) blends were prepared using REX and their mechanical properties tested resulting in an slightly improved elongation at break (10 *vs* 5 % for neat PLA) (58) and an enhanced crystallinity rate (22 *vs* 15 % for neat PLA) (58). These results confirm that while using a stoichiometric balance of monomers for the synthesis of PGS, a higher toughness of the PLA / PGS blend can be achieved. It is shown that higher M_w of the PGS enables entanglement with the PLA leading to a higher elongation at break and toughness (Figure 16). Combination of REX and a free radical initiator allowed the grafting and crosslinking of the PLA matrix forming PLA-*g*-PGSMA copolymers. For an effective toughening of PLA by reactive melt blending with glycerol-based polyesters, the best conditions found for the synthesis of PGSMA were 1 / 0.5 / 0.5 mol glycerol / succinic acid / maleic anhydride synthesized at 150°C for 5 h (58).

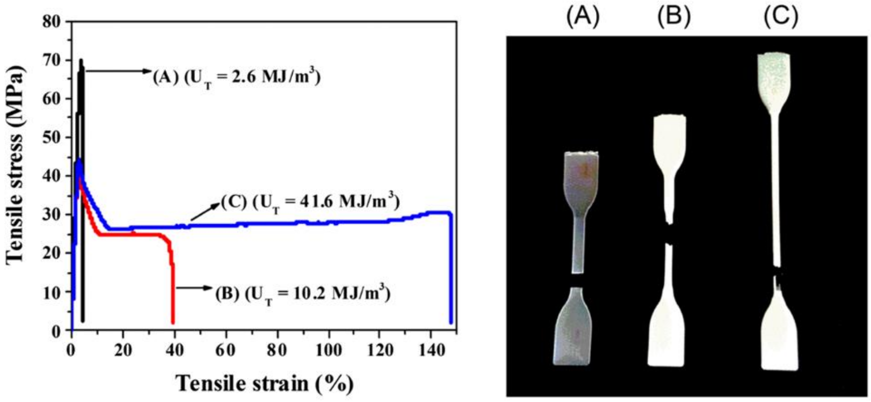


Figure 16 Stress vs strain curves indicating fracture toughness (UT) and appearance of (A) neat PLA, (B) 80/20 RPLA/PGSMA1 (reaction temperature = 180°C), and (C) 80/20 RPLA/PGSMA2 (reaction temperature = 150°C) (58)

Another way to compatibilize PLA with PGSMA is the use of dynamic vulcanization process.(45) This technique involves both the melt blending and the chemical reaction between PLA and a secondary polymer as well as the creation of a cross-linked elastomeric phase in the PLA matrix.(45) The preparation of the blends was done through reactive extrusion and cross-linking was initiated by Luperox101 peroxide. Different formulations of PGSMA were produced by varying glycerol, succinic acid and maleic anhydride amounts. This allowed the increase or decrease of unsaturation on the copolymer, which will affect the cross-linking density. Thus, it can be concluded that the main reactions taking place during the dynamic vulcanization of PLA and PGSMA are the PGSMA self-crosslinking and PLA-*g*-PGSMA formation. In addition, it was proven that a stronger interfacial adhesion was obtained with increasing of maleic anhydride amount due to higher PLA-*g*-PGSMA formation. Then a series of blends of PLA / PGSMA were obtained with a fixed of initiator of 1 % (note that a higher load of initiator did not improve the toughness). The tensile strength and modulus of the blends were decreased linearly with the addition of PGSMA due to its elastomeric properties. The blend of 60 / 40 PLA / PGSMA displayed an enhancement of 53 and 175 % on the elongation at break and notched Izod impact respectively as compared to neat PLA.(45)

6) Compatibilization induced by plasticizers

Piontek *et al.*(59) studied the compatibilization effect of bio-based ethylene-propylene-diene-rubber (EPDM) on PLA. The blends were prepared at different ratios of radical initiator (poly(ethylene-co-methyl acrylate-co-glycidyl methacrylate) (EMAGMA), soybean oil (SBO) or Tertbutylperoxy 2-ethylhexyl carbonate (TBEC) peroxide). The addition of EMAGMA increases phase compatibilization between the samples both with and without the TBEC. The authors claim that the peroxide decomposition and the radical reactions mainly take place in the PLA phase. Adding EMAGMA to the blends decreases the initial size of the soft phase and thus increases the interfacial area (Figure 17) where diffusion of the peroxide between the phases can take place. This phenomenon results from the inhibition of coalescence due to the addition of compatibilizer (Figure 17).

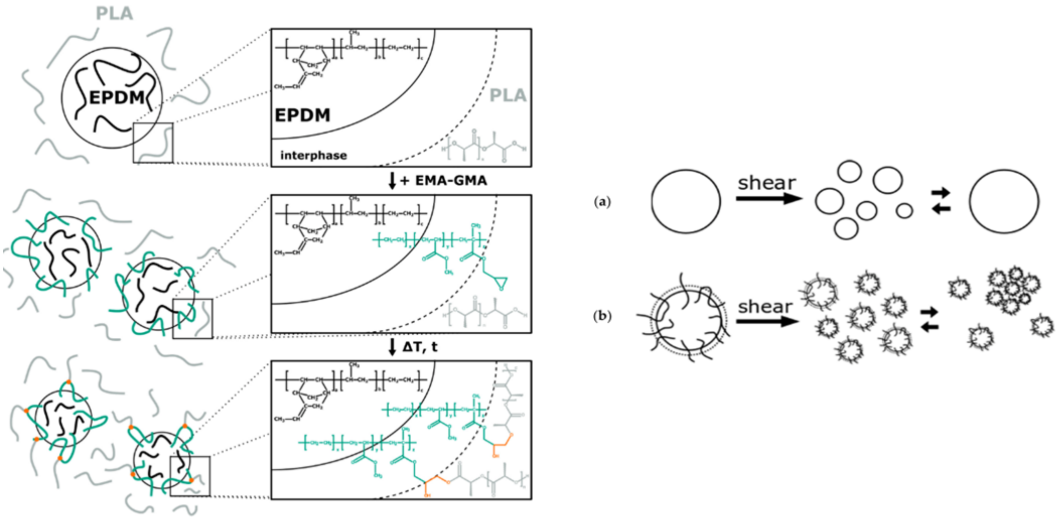


Figure 17 Schematic representation of physical compatibilization of PLA and EPDM with EMAGMA and possible chemical reactions and (a) coalescence of dispersed particles without compatibilizer and (b) inhibition of coalescence with compatibilizer and possible agglomeration (59)

The Young's modulus as well as the tensile strength decrease with increasing content of soft phase independent of TBEC content in the blends. The addition of peroxide increases the elongation at break compared to the reference samples. The elongation at break, at first increases with an increasing content of SBO of up to 20 wt % and then decreases for 30 wt % SBO in the soft phase. This increases the viscosity ratio *i.e.* the ratio between the viscosity of the dispersed phase (η_D) and the continuous phase (η_C), which favors droplet breakup of the soft phase leading to smaller particles and a higher elongation at break. However, while SBO can contribute to the EPDM crosslinking as a small multifunctional crosslinking agent, it can also decrease the crosslinking efficiency of EPDM by reacting with the free radicals without bonding to the EPDM phase. Favorable elongation at break were obtained for an optimum SBO content of about 20 wt % inside the soft phase.(59)

In order to compatibilize oligo(lactic acid) (OLA) with cellulose acetate (AC), plasticized copolymers were prepared by reacting EJ400, a diepoxide, with the OLA and AC via reactive extrusion (60). Initially two different compatibilizers containing 14 wt. % (C1) and 30 wt. % OLA (C2) were prepared. A ratio 4 / 1 (wt / wt) of pAC / compatibilizer blends were prepared beforehand at 230 °C and then blended with PLA at 197 °C in a second step. A consistent increase in torque with respect to the pAC can be observed and can be attributed to the capability of the partially unreacted EJ400 to further react with the pAC at 230 ˚C determining some occurrence chemical crosslinking which was confirmed by extraction with a solution of acetone / water (90 / 10), resulting in a residue of 8 and 11 wt% for the blend pAC/C1 and pAC/Clab1, respectively (60). Also because the OLA has one reactive site, a brush-type structure is expected, due to the ring opening of the diepoxide. The mechanical properties of the blends containing 85 % PLA show a decrease of Young's Modulus, when the amount of C1 compatibilizer is increased. In blends containing only C1, Young's Modulus is increased while tensile strength is decreased, attributed to the formation of interfacial interactions due to compatibilization (60).

The use of OLA was also studied by Garcia-Sanoguera *et al.*(61) in order to characterize the mechanical properties of polylactide blends. Therefore, PLA was blended with 10 wt% of OLA and various amounts of DCP (0.1 or 0.3 phr) or maleinized linseed oil (MLO) (3 or 6 phr). The results showed that with 0.3 phr of DCP the PLA/OLA blend exhibited an impact strength of 52 kJ/m^2 which represents 25% increase compared to neat PLA (61). On the other hand, the addition of MLO also provided an enhanced impact strength to the PLA/OLA blend *i.e.* 60 kJ/m^2. However both strategies led to a significant decrease of the crystallinity compared to neat PLA (61).

Addiego *et al.* studied plasticization of PLA with Acryl-PEG and the effect of reprocessing on the blends (62–64). Different blends were produced by REX: one blank (containing no acrylated poly(ethylene glycol) (acryl-PEG)) and one containing PLA / Acryl-PEG / L101 (79 / 20 / 1 wt%) (62–64). Then recycling-like drill were performed. In a first study, it was done via cycles of extrusion and injection molding (62) and a second work studied cutting / extrusion / compression-molding sequence (CM)(63) (Figure 18). In the first work, the molecular weights of both PLA and plasticized PLA (pPLA) decreases after reprocessing which is due to chain scission

(62). However, this effect is more pronounced for regular PLA, as for pPLA the formed shorter chains may act as plasticizers by increasing the chain mobility. For pPLA the ultimate strain (ε_u) increased from ε_u = 91% to ε_u = 127% after the fifth processing cycle (62).

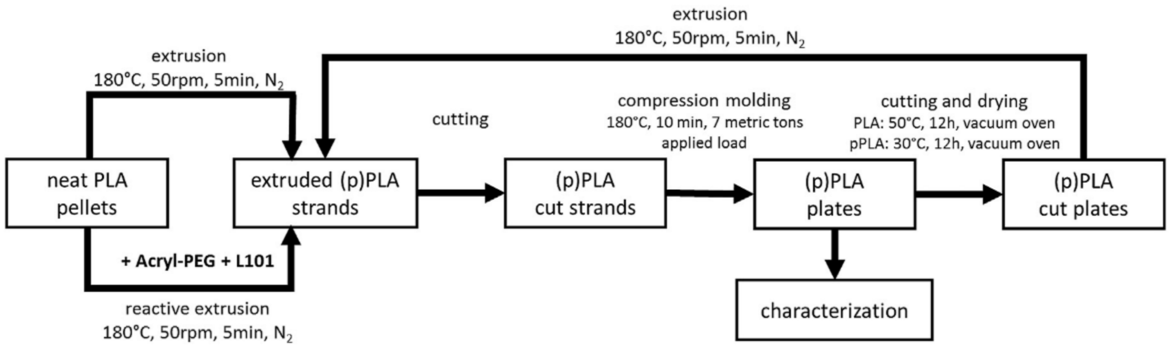


Figure 18 Processing and reprocessing procedures of (p)PLA including the main experimental conditions (63)

In the second work, the specimens were analyzed and characterized after 1 (CM1), 3 (CM3) and 5 (CM5) processing cycles. The plasticization of PLA decreased its tensile strength as a decrease of ultimate stress s_u from 71.9 MPa for PLA CM1 to 19.4 MPa for pPLA CM1, and the decrease of yield stress s_y from 77.9 MPa for PLA CM1 to 26.6 MPa for pPLA CM1 was observed (63). The main decomposition mechanism of PLA is random chain scission, which lowers its molecular weight (from 289 kg/mol to 154 kg/mol) and increases crystallization. However, for pPLA the decomposition mechanism is more complex. Indeed, the mechanical properties worsened (lower tensile ductility and decreased toughness) from the first processing to the third processing with the material becoming brittle. This can be explained via chain scission mechanisms of the polymer matrix where the polymer chains become shorter, due to transesterification, thus inducing higher crystallinity rates. This, in combination with the coupling of poly(acryl-PEG) phase size reduction and pore formation may decrease the physical interactions between the matrix and poly(acryl-PEG) which could be responsible for cracking. The authors note that at this stage plasticized PLA made by reactive extrusion cannot be repurposed (63).

The third study focused on the characterization of the formed chemical inclusions of PLA / acrylPEG / L101 (79 / 20 / 1 wt %).(64) The authors note that two reaction pathways are possible; the homopolymerization of acrylPEG or the grafting of acrylPEG onto PLA which could act as starting point for the polymerization of acrylPEG. The absence of two separate melting peaks in PLA/acrylPEG and pPLA supports the assumption of a good miscibility between the plasticizer and the matrix even after reactive plasticization. Grafted PLA / poly(acrylPEG) and plasticized PLA / poly(acrylPEG) show higher elongation at break compared to PLA >16 % (this is due to the limitation of the testing machine). Also the Young's modulus is decreased (7.5, 21 MPa for PLA / acrylPEG and pPLA, respectively) (64).

The same group also used myrcene (My) and limonene (LM) which are two bio-based plasticizers to assess processability and performance using both reactive extrusion and conventional blending (65). For the reactive extrusion, Luperox 101 was used to initiate radical formation. Various compositions were tested: PLA / (LM or My) / L101 were processed at different % mass ratio (100/0/0, 80/20/0 and 79/20/1). In presence of L101, two main reactions take place during the reactive extrusion: (i) the polymerization of the plasticizer itself or (ii) PLA branching. However, there is no direct proof of grafting of the plasticizers onto the PLA backbone. For the case of myrcene there is radical homopolymerization that is shown by a slight increase of M_w *i.e.* M_w = 229 kg·mol^{-1}) for PLA / My / L101 compared to M_w = 204 kg·mol^{-1} for PLA / My.(65) The author noticed an increase of the extrusion force for PLA / My / L101 compared to PLA / My as well as an increase of My inclusions size from PLA / My to PLA / My / L101 that seemed to witness the polymerization of myrcene (65).

7) PLA / PCL blend compatibilization

Shin *et al.*(66) studied the viscoelastic properties of PLA / poly(ε-caprolactone) (PCL) blends compatibilized by four different methods. The first two are based on reactive extrusion. The first method (Blend-1) involving dicumyl peroxide (DCP) creates free radicals on both PLA and PCL whereas the second one (Blend-2) uses Joncryl as compatibilizer. Both Blend-3 and Blend-4 are prepared according to the same extrusion parameters as Blend-1 and Blend-2. However, after extrusion, they were subjected to an electron beam irradiation that facilitate cross-copolymerization at the interface between PLA and PCL. The fourth method involved the use of a chain extender, nine glycidyl methacrylate, as the reactive compatibilizer. Well compatibilized blends could be distinguished using their viscoelastic properties. These blends had similar or higher G', G'', and η* values than those calculated using the log-additive mixing rule, whereas poorly compatibilized blends showed negative deviations of G' (except at low frequency), G'', and η* (Figure 19). In addition, poorly compatibilized blends exhibited a plateau region in tan(δ) curve and fast stress relaxation process (Figure 19) (66).

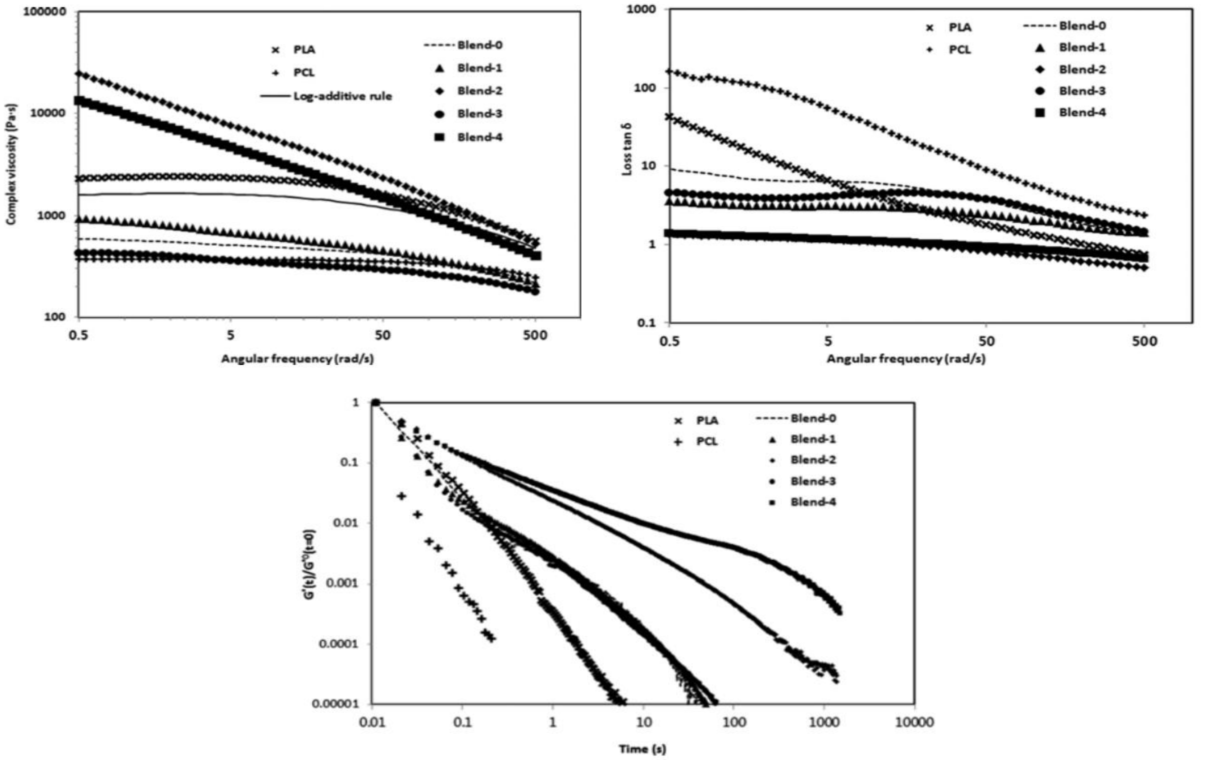


Figure 19 Complex viscosities as a function of angular frequency, tanδ curves as a function of angular frequency, normalized transient stress relaxation moduli, G (t)/G*0 (t=0), (measured at 190°C) for PLA, PCL, and compatibilized and non-compatibilized PLA/PCL (80/20) blends* (66)

With the use of proper additives, degradation of PCL / PLA (90:10) blends can be triggered by light irradiation *i.e.* it is also called photodegradation (67). The authors highlighted that the blends compatibilized with DCP and containing TiO_2 exhibited an enhanced photodegradation, 50% weight loss within 44 days in wet conditions and 30% weight loss within 77 days, compared to neat PLA. Therefore, it seems that Simon *et al.* achieved the development of photodegradable polyester blend (67).

8) Other blend compatibilization

The improvement of mechanical properties of PLA / COPUP (castor oil-based polyurethane pre-polymer) blends was performed by reacting isocyanide-terminated COPUP with the hydroxyl groups of PLA (68). Firstly, isocyanide-terminated COPUP was synthesized by reacting castor oil with methylene diphenyl diisocyanate (MDI). The COPUP was then blended at different weight percentages (5, 10, 20, 30 %) with PLA, the resulting blends were then subsequently injection molded (68). For the blend containing 30 % of COPUP, the elongation at break increased by 401.3 % compared to neat PLA while the tensile strength and Young's modulus decreased slightly with 61 (neat PLA) to 33 MPa (COPUP 30 %) and 2601 (neat PLA) to 1477 MPa respectively (68).

Another study from Athanassiou *et al*.(69) focused on the use of extrusion, compression molding and injection molding to produce blends of linear-PLLA with different weight percent of star-PDLLA. The aim was to use the amorphous star-PDLLA as plasticizer to improve the mechanical properties of linear-PLLA. Subsequently the blends (0, 10 and 20 wt % of star-PDLLA) were injection-molded at 190 °C in a dumbbell shape for mechanical testing. Blending of star-PDLLA resulted in less decomposition during processing compared to linear PLLA. This was observed for injection molding and extrusion (69). Moreover, the T_g decreased with increasing concentration of star-PDLLA, this would indicate that there is a plasticizing effect on the linear-PLLA matrix. Increasing the weight percentage of star-PDLLA, increased the toughness for both extruded/compressed and injected products (increase of 222 % and 265 %, respectively). While Young’s modulus decreased slightly from 1.9 GPa for injection molded PLA to 1.7 GPa for 20 % star-PDLLA (−10 %) and from 1.7 GPa for EC (extrusion and compression molded PLA) to 1.5 GPa for 20 % EC star-PDLLA (−12 %) (69).

The production of poly(lactic acid) and (poly(ω-hydroxytetradecanoic acid)) (PC14) block copolymers was achieved by a transesterification reaction using $Ti(OBu)_4$ as catalyst (70). The objective was to improve the elongation at break of PLA. Parameters such as screw speed, residence time, reaction temperature and PLA / PC14 blend ratio were varied in order to find the best conditions to improve the elongation at break of the resulting material. Variation of the screw speed was investigated while keeping, temperature (200°C), residence time (30 min), catalyst concentration (200 ppm $Ti(OBu)_4$) and blend ratio (PLA / PC14 (90/10 w/w)) constant. It is shown that screw speed higher than 150 rpm induces a decrease of the molecular weight due to chain scission (70). Studies on the effect of reaction time indicated that; 15 min reaction time yields the highest elongation at break, an increase of the residence time lowers the molecular weight (280 kg/mol after 5 min down to 250 kg/mol after 15 min) (70) and increase the elongation at break (50 % after 5 min up to 145 % after 15 min) (70). Furthermore, PLA / PC14 blends prepared by REX (200°C, 150 rpm, 15 min residence time) containing 20 % of PC14 exhibits an impact strength increased by 2.4 times compare to neat PLA (70).

Mihai *et al.*(71) studied the behavior of plasticization of PLA using a bio-based cardanol derivative. This derivative, made by epoxidation of cardanol, is grafted through reactive extrusion and is that case, ethyltriphenyl phosphonium bromide (ETPB) was used as catalyst. Different blends were elaborated by varying the amount of ECard and ETPB. The absence of ETPB show incompatibility between PLA/ECard as large domains (- 5 µm) are formed as seen by the SEM analyses. The reaction between ETPB and PLA end groups allows better compatibilization, however the addition of more than 0.02 phr of catalyst deteriorates the overall properties of PLA. Thermal stability is affected only at temperatures above 270 °C which do not interfere with the processing temperatures. The best results were obtained for PLA / Ecard / ETPB (80 / 20 / 0.02 phr) which has a 49 % increase in elongation at break (71).

PLA / PBS blends were compatibilzed in another work, by adding poly(propylene carbonate) grafted maleic anhydride (gPPC) (72). Different blends were produced by varying the content of gPPC to evaluate the different effects (72). Various compounding conditions were assessed for each blend by changing the specific mechanical energy (SME), which is defined as the energy given to the system during the reactive extrusion. This value depends on the flow rate, screw speed, the motor power, and torque (commonly used parameters). It was shown that high shear rates combined to short residence times was able to allow chemical reaction while preventing thermal decomposition of the reagents (72). Moreover, it promoted the reduction of the droplets size in all the blend allowing energy dispersion. In some cases, strain at break was increased up to 360 % compared to the neat blend (72).

A study reported the production of ternary blends PLA / PBS / ethylene-methyl acrylate-glycidyl methacrylate (EGMA) which were then compression molded into dumbbell shaped specimen (73). The goal of this paper was to study the influence of EGMA on both PLA / PBS blends morphology and mechanical properties. It is shown that the addition of 30 wt % of PBS in the PLA matrix does increase the elongation at break (ε = 336 %) but result in a decrease in tensile strength (σ = 40 MPa). When the compatibilizer EGMA was added to a PLA/PBS blend, the tensile strengths decreased from 37 to 24 MPa for samples 5 and 20 wt % EGMA, respectively. On the contrary, the elongation at break of blends has a remarkable increase from 478 % for 5 wt % EGMA to a maximal value of 549 % for 10 wt % EGMA and exhibits superior stretchability of 83 times higher than that of neat PLA, which represents enhanced ductility. With further increase of EGMA contents to 15 wt % and 20 wt %, the elongations at break slightly drop to 417 and 324 %, respectively. With the incorporation of 20 wt % EGMA, the impact strength was improved to 46.5 kJ/m^2 which is approximately 20 times more than PLA (73).

Palai *et al.*(74) prepared blown films of PLA / TPS (thermoplasticized starch). Two different starch sources were used: Cassava and Maize starch. TPS was obtained by mixing the starch with 25 % glycerol and 5 % water in a Rheomix at 120 °C. The PLA / TPS blends were prepared by reactive extrusion and compatibilized using glycidyl methacrylate (GMA) by mixing the TPS with PLA, GMA and benzoyl peroxide as radical initiator. Blends with a concentration of TPS from 5 to 30 % weight decreased the tensile modulus both in transverse direction and machine direction having 50 % value of virgin PLA for blends containing 30 % TPS. On the contrary, increasing the TPS concentration, elongation at break increased up to 144 % for blends containing 30 % TPS. PLA containing thermoplasticized cassava starch display better tensile properties compared to maize starch. This may be due to the higher crystallinity of thermoplasticized cassava starch evidenced by FTIR and DSC analysis (74).

In a recent study, Fredi *et al.*(75) investigated the compatibilization with Joncryl ADR 4468 of PLA / poly(ethylene 2,5-furanoate) (PEF) blends that aimed to be used as sustainable packaging. Several formulations were produced by melt compounding and hot pressed to obtain polymer films. Joncryl was proved to effective both as a chain extender and a compatibilizer leading to a more homogeneous PEF domain size in the PLA matrix. However, 10 wt% of PEF (PLA-PEF10) were proved to increase the crystallinity of the blend up to 28 % (+ 72% compared to neat PLA), the addition of 1 phr of Joncryl (PLA-PEF10-J1) had the opposite effect leading to a crystallinity of 11% (- 34 % compared to neat PLA). (75) The mechanical characterization of the different synthesized blends proved the positive effect of Joncryl. Indeed, the uncompatibilized blend displayed mechanical properties that were lower to those of neat PLA. But the PLA-PEF3-J1 blend (3 wt% of PEF, 1 phr of Joncryl) displayed highly improved strain at break and tensile strength (+103 % and +42.5 % compared to neat PLA respectively) even if the elastic modulus was slightly hindered (-11 % compared to neat PLA). Finally, the authors proved that with only 1 wt% of PEF both UV- and oxygen-barrier were enhanced which represent an interesting point in order to use those blends in the packaging industry. Therefore, PLA-PEF blends compatibilized with Joncryl represent interesting materials yet the ideal blend has not been found. Indeed, the blends that displays the best gas barrier is not the one with the best mechanical properties of the highest crystallinity.

All the studies of this part explore various way to compatibilize PLA-based blends and focus mostly on the improvement of the mechanical properties of PLA. It would be interesting to go further and study deeper both thermal properties and fire behavior of the blends. It may open a wider range of application for the developed polymers. Moreover, focusing on the development of bio-based compatibilizers for bio-blends (*i.e.* PLA / biopolymer blends) would bring new insight on finding alternatives to petroleum-based polymers.

3. Composite Compatibilization

Currently most of the composites on the world market are based polymers arising from petroleum based polymers *e.g.* polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC) (76). However, the interest to recycle these composites keeps growing resulting in the need of greener products. Thus combining the creation of green composites to mechanical properties (impact strength, ductility or tensile strength) enhancement strategies, PLA can be mixed with fillers. Therefore research strategies such as the use carbon derivatives (17,77–79), reusing food byproducts (76,80–84) or wood derivatives have been employed (85–90).

1) PLA / Carbon fibers or carbon nanotubes composites

PLA-*g*-MAH was proved to be a good compatibilizer for PLA-based blends (45,47,50,52,55,58,72) but it can also compatibilize PLA / natural fibers composites as mentioned in Pérez-Fonseca *et al.*(17) review's or PLA / carbon fibers composites. The grafting of PLA with MAH can be performed using dicumyl peroxide as an initiator (77). The resulting compatibilized composites displayed improved mechanical properties with a 150 % and 28 % enhancement in tensile modulus or impact strength respectively. Moreover, the addition of 0-3 % wt PLA-*g*-MAH as compatibilizer increased the crystallinity and displayed a surface resistivity of 10^{-3} Ω.cm (77). PLA properties were improved by the addition of carbon nanotubes (CNT) using PLA-g-

MAH (78). The latter was obtained) by REX using benzoyl peroxide (BPO) as a radical initiator prior to be mixed with PLA. The obtained nanocomposite displayed an impact strength enhanced by 274 % with 1 wt % of CNT and 3 wt % of PLA-*g*-MAH (78). Moreover, the TGA results showed that the addition of CNT and PLA-*g*-MAH does not affect the thermal properties of PLA (78).

Aytac *et al.*(79) studied the influence of 3 or 5 wt% of non-functionalized (MWCNT), hydroxyl-functionalized (MWCNT-OH), carboxyl-functionalized (MWCNT-COOH) and polycarbonate-grafted multi-walled carbon nanotube (PC-g-MWCNT) on the properties of polycarbonate (PC) / PLA (70 / 30 wt%) blend (79). The results showed that MWCNT-COOH contributes to enhance the mechanical properties of the PC / PLA blend *i.e.* the elongation at break was increased up to 159% *vs* 7.6% for neat PLA (79). On the other hand, the addition of 5 wt% of PC-g-MWCNT influenced the electrical conductivity of the PC / PLA blend (Figure 20).

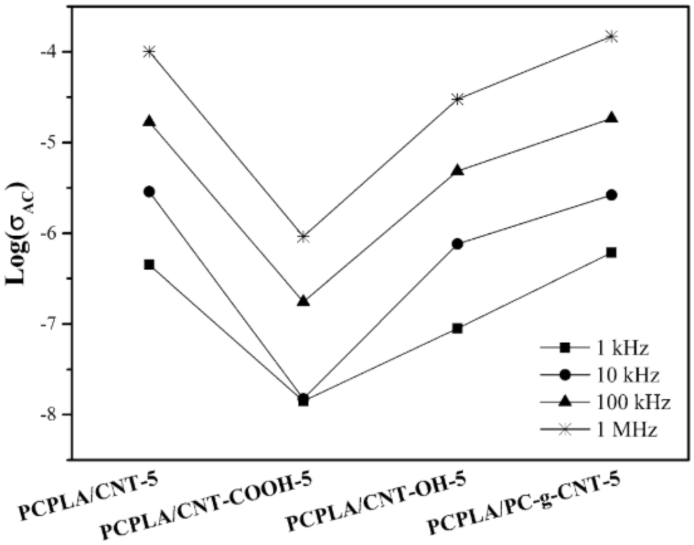


Figure 20 Log (σ_{AC}) of nanocomposites at different frequencies (79)

2) PLA / food industry byproduct composites

Different studies have focused on the production of biocomposites from the combination of PLA with wastes from the agro-food industry, multi-functionalized vegetable oils (80–82) or wood flour (76,83,84).

The composites prepared with wood fibers are well known under the name of wood-plastics composites (WPCs), and a lot of applications with PP, PE and PVC have been developed (83). Furthermore, since PLA displays some properties that are equivalent to those of oil-based polymers, WPCs based on PLA and wood flour represent a promising biodegradable material with good mechanical properties for industrial applications *e.g.* food packaging. Gu *et al.*(83) developed PLA / wood flour (WF) composites modified with MAH by a one-step REX process. As mentioned before, MAH acts as a compatibilizer and provides an efficient grafting and crosslink between the three components of the composite (Figure 21). It was observed that 1 wt % of MAH in the composites increase the mechanical strength up to 144 % whereas the tensile strength is increased by 44 %. However, according to thermal analysis, the addition of MAH and dicumyl peroxide (initiator), during the REX process catalyzes decomposition of PLA (83).

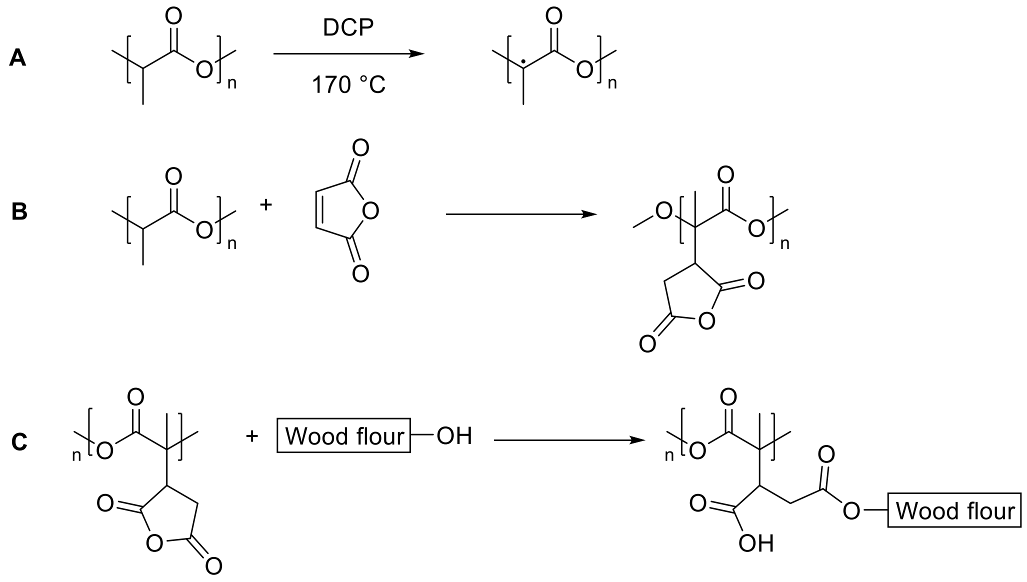


Figure 21 Mechanism of chemical reaction among PLA, wood flour and MAH (83)

The development of PLA / WF composites was also studied by Zhang *et al.*(76) with benzoyl peroxide (BPO) as the initiator and methyl acrylate (MA) as the compatibilizer. After grafting wood flour with MA, WF-g-polymethyl acrylate (PMA) was used as a filler to improve the interactions between PLA and WF (76). An enhanced interfacial compatibility of the composites treated with MA and an improved water resistance were observed. However, the thermal stability of the compatibilized composites was slightly lower than that of pure PLA (76). Another type of compatibilizer based on methylenediphenyl diisocyanate (MDI) combined to MAH was studied by Seo *et al.*(84) and used with PLA / polybutylene succinate (PBS) / WF composites. The DSC thermograms showed that MDI contributes to the increase in T_g of the composites

(84). Moreover, the composites containing both MDI and MAH displayed the most enhanced thermal stability (84).

Quiles-Carrillo *et al.*(80–82) published two studies using food industry by-product : one on PLA / almond shell flour (ASF) compatibilized with maleinized linseed oil (MLO) and one relating to the compatibilization of PLA / orange peel flour (OPF) by acrylated epoxidized soybean oil (AESO). The addition of high amounts of ASF in the PLA matrix enhanced the hardness of the resulting bio-composites (81). Through a plasticizing effect and grafting, MLO was able to improve the compatibility between PLA and ASF (81). Therefore, the mechanical, thermal and thermomechanical properties of PLA / ASF composites displayed strong enhancements compared to the uncompatibilized composite (81). Indeed, with a MLO content of 10 parts per hundred resin, T_{deg} of PLA / ASF composite was measured around 327°C with a residue of 0.7 % (81). In comparison, the PLA / OPF composites containing 10 % of OPF and compatibilized with AESO displayed a decomposition temperature of 330°C with a residue of almost 11 % (80).Both decomposition temperatures of the composites are close to that of neat PLA but the residue is higher especially for PLA / OPF compatibilized with AESO (80,81). Another food industry recoverable waste, walnut shell flour (WSF), was used to develop a PLA / PCL / WSF composite compatibilized with MLO (82). However, these composites displayed an improved ductility (elongation at beak up to 19 *vs* 9 % for neat PLA) (82) especially with low levels of WSF (10-20 %) (82), due to the presence of PCL, and minimal losses in terms of mechanical toughness (shore hardness around 74-78 *vs* 81 for neat PLA) (82) and mechanical stress *i.e.* impact strength comparable to neat PLA when WSF content less than 30 % (82), the TGA analysis showed lower decomposition temperatures compared to neat PLA but higher residues (~10 %) (82).

3) Biobased nanocomposites (PLA / CNC or SNC, PLA / CNF)

Arising from renewable biomass sources, cellulose nanocrystals (CNC) are manufactured by extracting the crystalline part of cellulose. CNCs display improved mechanical properties including high tensile strength and elastic modulus (140-220 GPa) making them an attractive material for PLA-based nanocomposites, however the compatibility between PLA and CNCs needs to be improved. Dhar *et al.*(85,86) investigated a single step REX process designed to produce PLA grafted cellulose nanocrystal (PLA-g-CNC) (Figure 22). The aim of this work was to develop nanocomposite films for packaging application. The grafting of PLA on CNC was performed via REX make the hydrophobic PLA and the hydrophilic CNC compatible.

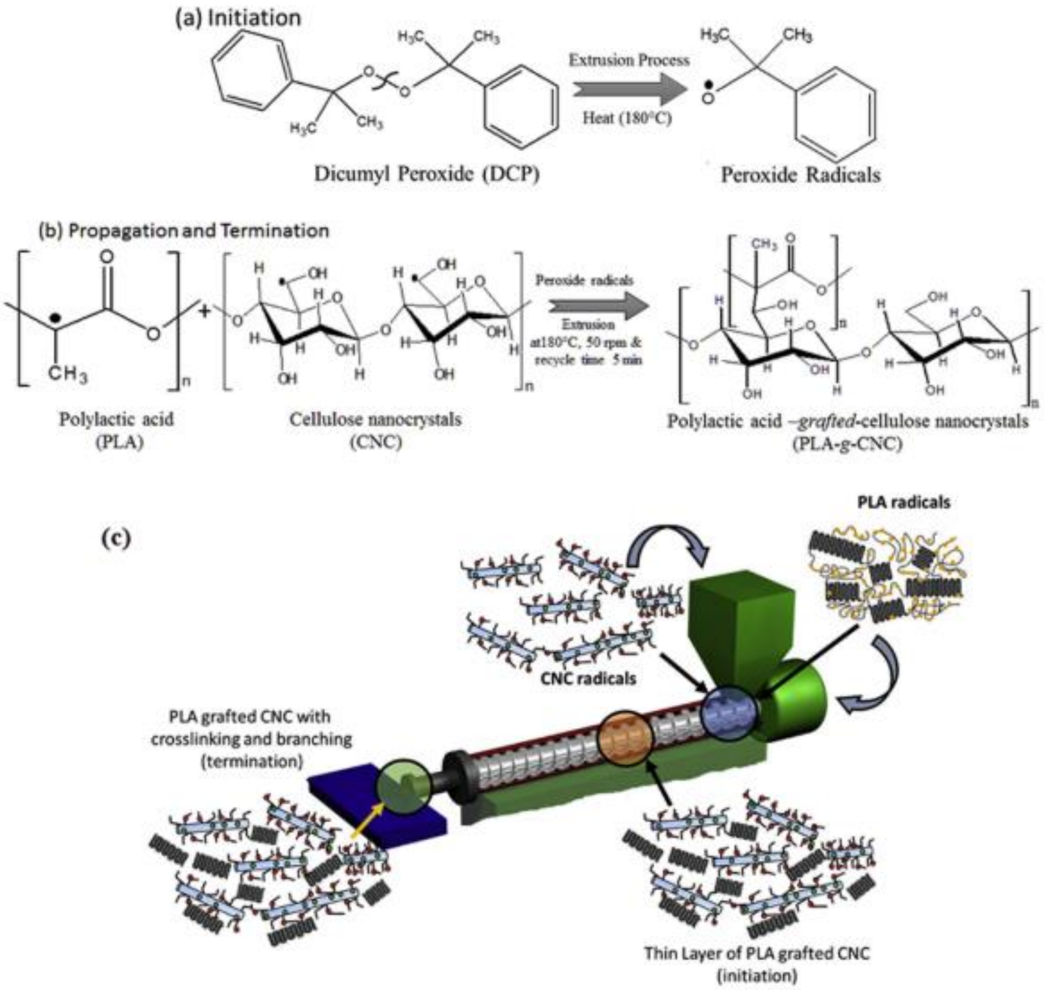


Figure 22 (a) Mechanism of thermal decomposition of the DCP into peroxide radicals during extrusion at T ¼ 180°C (initiation step), (b) Generation of CNC and PLA radicals followed by reactive extrusion at screw speed ¼ 50 rpm and recycle time ¼ 2 min (propagation step) leading to the formation of PLA grafted CNC structures (termination step). (c) Pictorial representation of the grafting mechanism of initiation, propagation and termination of the reactive extrusion process for PLA-g-CNC along the different zones of the extruder (85)

One of the first study showed that the recycling of PLA-g-CNC nanocomposites was possible without significant breakage in the molecular structure of PLA *i.e.* no significant reduction of M_w was observed (Figure 23). Moreover, the M_w and M_n of PLA-g-CNC were significantly increased by the chain extension and the formation of branched structure. It was also proven that the presence of C-C bonds with the CNCs improved thermal properties and mechanical properties of the PLA-g-CNC composites. The tensile strength of the composite was increased by 41 % and Young's modulus enhanced by 490 % (85).Another study showed that PLA chains grafted onto

CNCs were responsible for the formation of high molecular mass (M_w ≈ 150−245 kDa) cross-linked structure (86). The obtained polymers displayed an improved processability as well as enhancement in the structural and barrier properties that present interests for potential applications in the packaging industry (86).

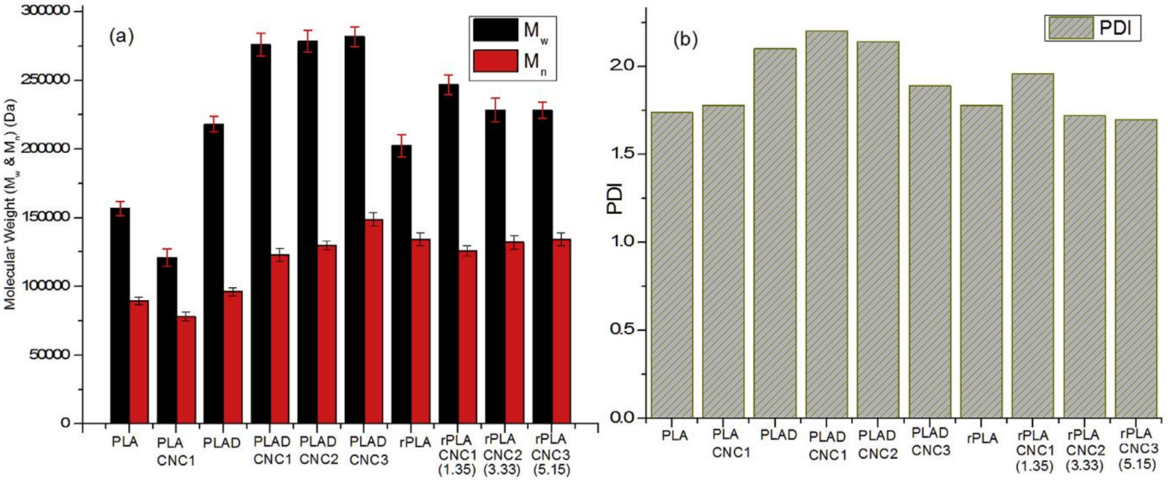


Figure 23 (a) Molecular weight distribution, weight average (Mw) and number average (Mn) and (b) polydispersity index (PDI) of extruded PLA, reactively extruded PLA/CNC nanocomposites (PLAD, PLADCNC1, PLADCNC2 & PLADCNC3) and reprocessed PLA-g-CNC gels (rPLA, rPLACNC1(1.35), rPLACNC2(3.33) & rPLACNC3(5.15)) (85)

The use of cellulose nanocrystals to reinforce PLA-based nanocomposites was also reported by Frone *et al.*(91) and Phuong *et al.*(92) PLA / polycarbonate (PC) blends can be modified with regenerated cellulose fibers to produce reinforced composites. Phuong *et al.* conducted the extrusion of a PLA / PC polymer reinforced with fibers in the presence of triacetine and tetrabutylammonium tetraphenylborate, as the transesterification catalysts (92) Infrared analysis showed that the catalyzed process allowed the grafting of PLA and PC onto cellulose fibers. Moreover, TGA analysis results displayed an improved thermal resistance for the composites resulting from the catalyzed process. These enhanced thermal properties were due to the grafting of PLA and PC onto cellulose fibers. Indeed, new chemical bonds were created between the matrix and the regenerated cellulose, displaying a compatibilizing effect on the resulting composite (92). More recently, Frone *et al.* reported the development of a single step process using dicumyl peroxide (DCP) as a cross-linking agent. They compared the extrusion technique to compression molding and 3D printing. First, the cross-linking agent promoted a better dispersion of CNC in the PLA/PHB matrix.

Moreover, the nanocomposites treated with DCP displayed the best thermal stability as well as the highest maximum decomposition temperature (91). The results of the DSC analysis show that CNC and DCP improved recrystallization. The nanocomposites obtained by REX had an increased crystallinity due to the process itself and an increased storage modulus. According to their study, Frone *et al.* discover that filament of PLA / PHB nanocomposite meet the standards required in the 3D printing applications, especially in terms of strength and thermal stability (91).

Silk nanocrystals (SNCs) were observed to thermally stabilize PLA when submitted to multiple extrusion processes (93). Moreover, SNCs help to strengthen PLA and contains serine groups which may form radical if initiated. Tesfaye et al.(93) used the peroxide-initiated REX process to perform the grafting of SNCs onto PLA. They obtained cross-linked PLA grafted SNCs. The existing of a bond between PLA and SNCs were evidenced by ^{1}H NMR. The rheological properties of the composite e.g. zero shear viscosity, storage modulus, crossover point were all improved by the addition of SNC increasing the ability of PLA to endure reprocessing (93).

Cellulose nanofibers (CNF), arising from renewable resources, are used as reinforcement for biopolymers such as PLA. Li *et al.*(94) studied the grafting of PLA onto CNF with the help of DCP (Figure 24) which led to an improvement of the interfacial interactions between the polymer matrix and the reinforcement fibers. Therefore, compared with uncompatibilized PLA / CNF nanocomposites, the PLA grafted CNF (PLA-g-CNF) displayed enhanced mechanical properties as well as a higher crystallinity rate (40% *vs* 35%). Indeed, the tensile modulus of PLA-g-CNF produced with 1 phr of DCP was increased by 1,400 MPa and its tensile strength by 12 MPa. It also has to be noticed that these values were much higher than those of neat PLA. Thus, it seems that the addition of DCP to PLA / CNF composites is a way to improve their mechanical properties which is viable from an industrial point of view (94).

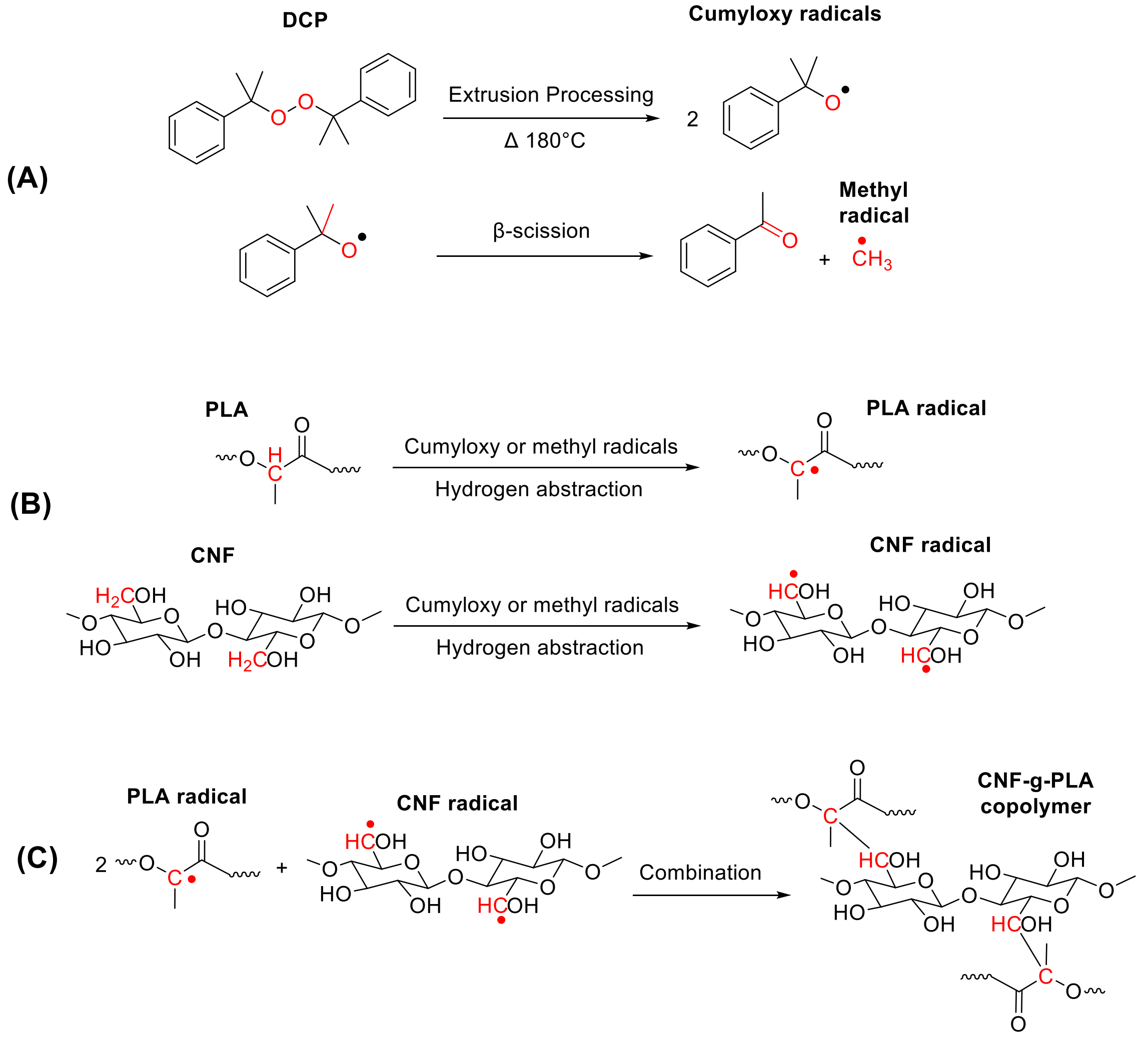


Figure 24 Possible reaction mechanism of DCP-initiated grafting of PLA onto CNF (94)

4) PLA / lignin or tannin composites

It has been proved that phenolic compounds usually display interesting properties including anti-UV capacity, thermal stability and flame retardancy (87,88). Especially, condensed tannins are abundant in bark and one of the most important phenolic compounds after cellulose, hemicellulose and lignin (87–90). Both tannin and lignin are bio-based and contain hydroxyl groups that can react with carboxyl terminal group of PLA. Thus, there has been great interest in producing biocomposites based on PLA and lignin or tannin. Zhou *et al.*(87,88) published the compatibilization of PLA and tannin via a one-step REX process (88) (Figure 26) and also worked on the interfacial improvement of PLA / tannin acetate (AT) biocomposites (87). The PLA / tannin composites were compatibilized with the help of promoters such as MDI or 3-aminopropytriethoxysilane (APS) which led to the formation of cross-linked tannin as well as tannin grafted PLA (88). The obtained composites displayed improved tensile strength (60 *vs* 50 MPa for neat PLA) and Young's modulus (55 *vs* 47 MPa) resulting from enhanced interfacial interactions between PLA and tannin (88). Moreover, the use of MDI helped to obtain higher melting temperature and onset of thermal decomposition compared to composites prepared with APS. However, the onset decomposition temperature of the composites prepared with MDI was slightly lower than that of neat PLA (319 *vs* 323 °C) (88). It can be noticed that the addition of tannin to PLA led to a char formation at temperatures around 350 °C (88).

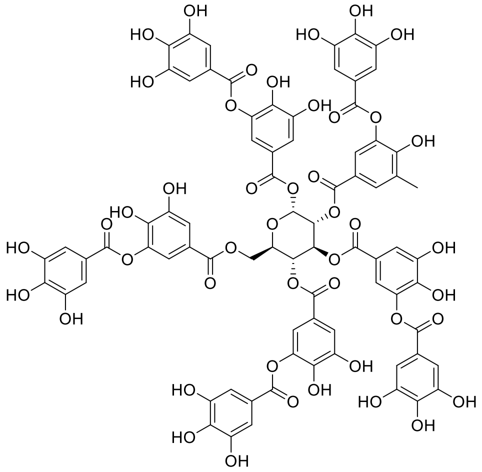


Figure 25 Tannic acid, a specific compound from the tannin family; is widely applied to any large polyphenolic compound containing sufficient hydroxyls and other suitable groups (such as carboxyls)

In another work from Zhou *et al.*(87) the REX process was used to compatibilize PLA / AT biocomposites with dicumyl peroxide (DCP). They achieved good interfacial interactions between AT and PLA as the onset decomposition temperature of the composite was comparable to that of neat PLA (87). It appears that the free radical compatibilization using DCP is more efficient for PLA / tannin composites. Compatibilized PLA / AT composites also displayed an enhanced hydrophobicity and, thus, may be use in the packaging industry (87).

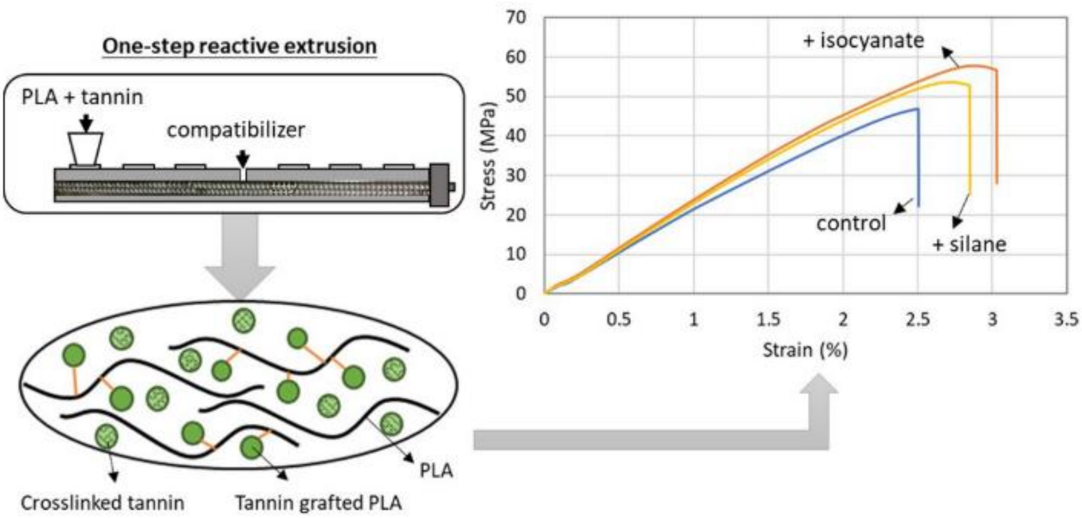


Figure 26 Production of tannin-grafted PLA via REX (88)

As already mentioned, lignin can also be added to PLA to produce biocomposites (89,90). Weng *et al.*(89) evaluated the properties of PLA / lignin composites with and without a silane coupling agent of γ-(2,3-epoxypropoxy) propy trimethoxysilane (KH560). The results showed a better adhesion between PLA and lignin in the composites thanks to KH560 that acted as a compatibilizer. The TGA of PLA / LG composites compatibilized and uncompatibilized displayed interesting results. The compatibilized composites containing 5 % of lignin started to degrade at lower temperature compared to neat PLA ($T_{5\,\%}$ = 297 *vs* 327°C for neat PLA) but it has a higher carbon residue (6 *vs* 1 %) (89). In their work, Abdelwahab *et al.*(90) used organosolv lignin (OL) that is lignin pretreated with organic solvent to design a PLA-based composite that may become an alternative to EPDM elastomer. OL displays a higher number of functional groups as well as a lower glass transition temperature compared to untreated lignin (90). This research focused on the toughening of PLA with OL in the presence of poly(vinyl acetate) (PVAc) and glycidyl-methacrylate monomer (GMA). The addition of PVAc enhanced the miscibility between PLA and OL which was confirmed by a single T_g at the DSC analysis (90). The lower T_g of the composites was an indicator of an enhanced flexibility and molecular mobility. The composite PLA / PVAc / OL / GMA (40 / 22.2 / 21 / 16.8 wt.%) composite with displayed the best mechanical properties : a high impact strength of ~900 J/m and elongation at break of 340 % however its thermal properties were lower compared to neat PLA (90).

5) PLA / thermoplastic starch composites

The blending of PLA with thermoplastic starch was studied by different groups (95,96). Bher *et al.*(95) produced PLA / thermoplastic cassava starch (TPCS) functionalized with graphene (GRH) nanoplatelets nanocomposites using REX. The compatibilization between TPCS and PLA was promoted by the incorporation of MAH and a peroxide initiator during the extrusion process. Compared to neat PLA, PLA-g-TPCS-GRH displayed a toughness enhanced by 900 % and an increased elongation at break (95). Moreover, the thermal properties of PLA-g-TPCS-GRH were similar to those of neat PLA. It was illustrated by the values of onset decomposition temperature of 309°C vs 319°C (95).

PLA / thermoplastic starch (TPS) filled with nanoclays were developed by Mekonnen *et al.*(96) in order to obtain multilayer films (Figure 27) that display improved barrier properties to both gas and moisture. Therefore, TPS was maleated to obtain maleated TPS (MTPS). It helped to improve the interfacial interactions between TPS and both nanoclays and PLA. In comparison to neat PLA, the obtained multilayer film displayed an oxygen permeability decreased from 0.260 down to 0.008 cm^3.m/m2.day.Pa and a water vapor permeation at 7 days of 1.10^{-13} kg.m/s.m^2.Pa which is 10 times lower than the one of neat TPS.

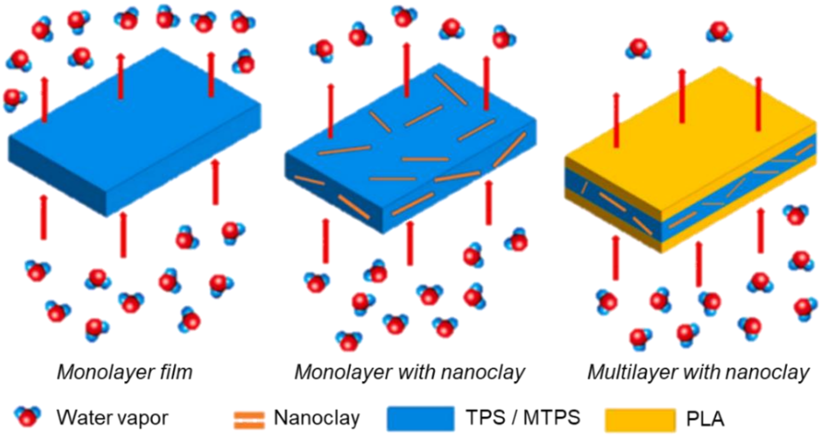


Figure 27 Illustration of proposed permeation mechanism through TPS / MTPS and TPS / MTPS with nanoclays and PLA coating (96)

6) Other composites

PLA was blended with other polymers and the addition of fillers or nanofillers to the blend in order to produce composites or nanocomposites that overcome PLA's weaknesses was studied. In particular the use of clays is present in some studies

(97,98). Cailloux *et al.*(97) used organically modified montmorillonite (o-MMT) to reinforce PLA via REX with and without SAmfE. Through REX, a good distribution of o-MMT in the PLA matrix was achieved and the SAmfE molecules helped to get a better clay delamination and intercalation resulting in improved interactions in the polymer matrix (97). The addition of o-MMT to PLA increase the onset decomposition temperature of the resulting composite of 10 °C compared to neat PLA (98). This study of Carrasco *et al.*(98) highlight the thermal stability enhancement properties of nanoparticles. Moreover, they investigated the kinetics of the thermal decomposition of PLA and PLA/o-MMT produced by REX. The TGA results confirmed the protective effect of nanoparticles against thermal decomposition (98).

The same group, in previous works, showed that PLA / BioPA blends with 30 wt% presented a brittle-to-ductile transition (99) as well as a higher activation energy of thermal decomposition (204 kJ/mol) (100). However, the immiscibility between PLA and PA required the use of a compatibilizer. Therefore, SAmfE was used to modify the rheological properties of PLA by REX in order to compatibilize PLA / polyamide 10.10 (BioPA) blends (70:30 wt%)(101) that were used to fabricate microfibrillated composites by fused filament fabrication (Figure 28). The authors observed that the addition of 1.25 wt% of SAmfE helped to influence the morphology of the PA microfibers, witnessing the compatibilizing effect of SAmfE. Moreover, the compatibilized blends seems to display an enhanced fracture toughness at high strain rates. Indeed the fracture parameters determined by applying LEFM (Linear Elastic Fracture Mechanics) showed that despite of a comparable K_Q, the G_Q (4.8 *vs* 3 kJ/m^2) and w_f (7.8 *vs* 1.5 kJ/m^2) of the blend containing 1.25 wt% of SAmfE were higher than those of neat PLA (101). To go further in the research it would be interesting to design a process that only use the extruder of the 3D printer to perform the reactive extrusion, the melt blending and the 3D printing.

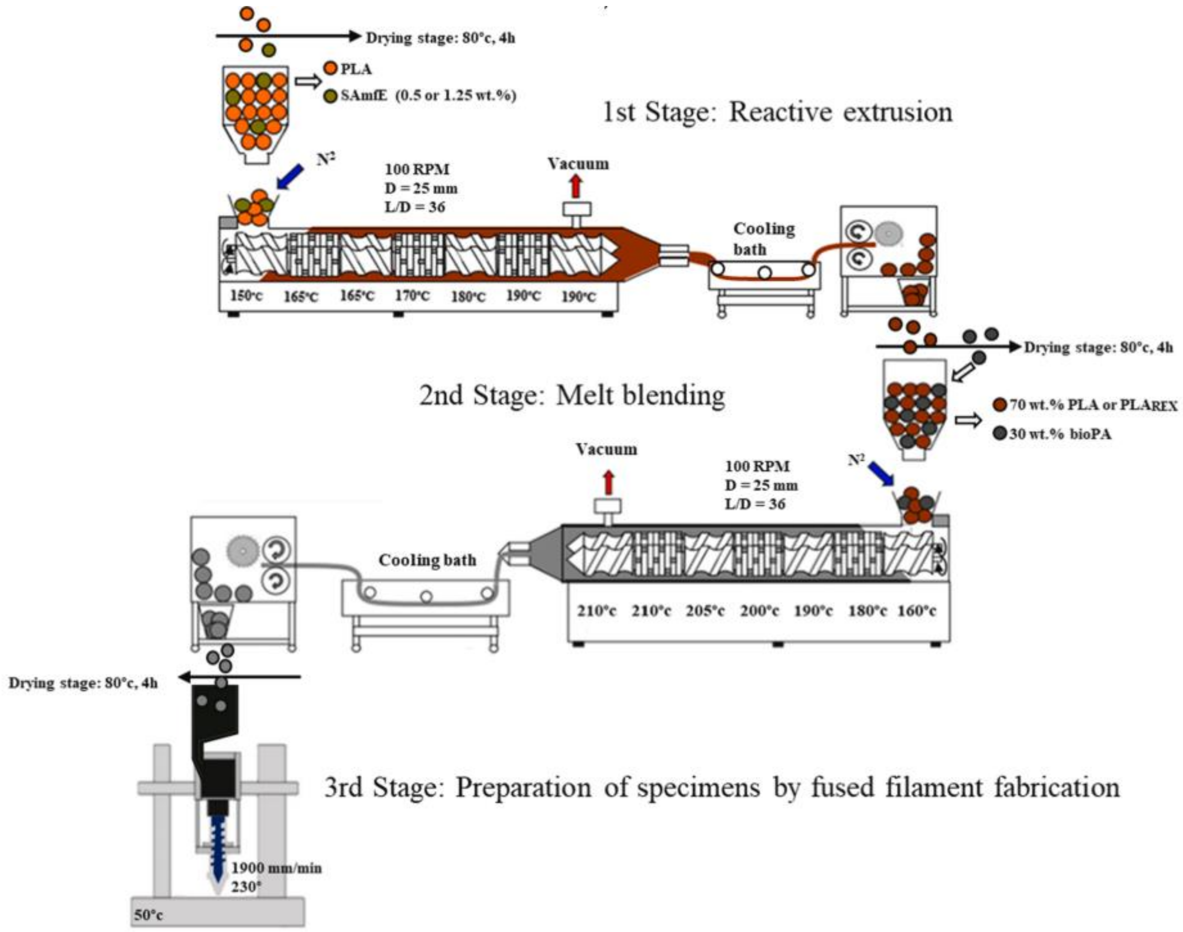
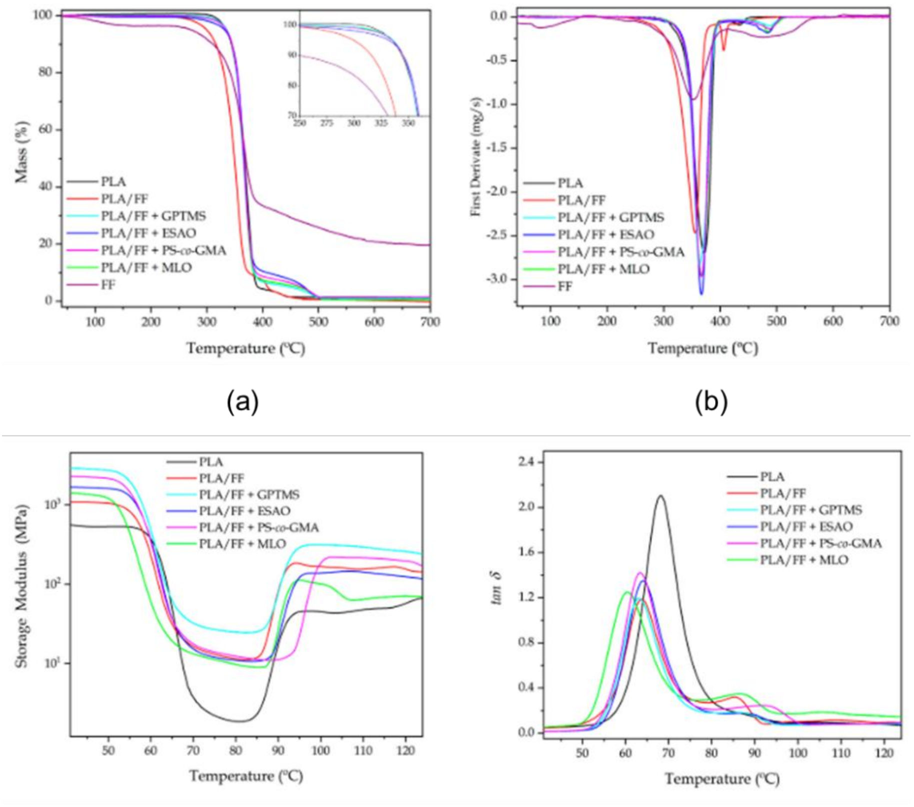


Figure 28 Schematic diagram of the manufacturing process including main manufacturing conditions per stages (101)

Talc is a commonly used filler in numerous industries. When added to PLA, lamellar talc allows the polymer to meet the requirement of the packaging industry for hot food solutions and of other consumable goods that need an improved thermal stability in terms of melt behavior and crystallinity (102). Barletta *et al.*(102) used modified lamellar talc with maleic anhydride (MAH) and glycidyl methacrylate (GMA) as compatibilizer to produce PLA/talc biocomposites via REX. The resulting compound had an improved processability without a worsening effect on the biocomposites properties compared to neat PLA (102). Also using talc as a filler, Nanthananon *et al.*(103) developed, via REX, hybrid composites of talc reinforced PLA and short-fibers with and without compatibilization. As expected, interfacial interactions between PLA and fibers were better in the presence of compatibilizer which led to improved properties of the resulting composite (103).

Zhang *et al.*(104) studied the role of Joncryl ADR 4468, MDI type TPU elastomer and micro-sized talc on both mechanical and crystalline properties of PLA-based composites. Joncryl acted as a chain extender (CE) introducing crosslinking and grafting which lead to an improved rigidity of the composite as well as an enhanced strength. Moreover, because of its miscibility with PLA, the TPU introduce both toughness and ductility of the resulting composite. Finally, their work highlighted the fact that talc helped to increase by 20% the crystallinity compared to neat PLA and it showed that the cold crystallization temperature was increased by 10°C (104). Therefore, it seems that this combination of additives can be used in order to develop PLA-based composites with enhanced strength, toughness, crystallinity and faster cold crystallization (104).

Flaxseed fibers (FFs) derived from linen waste may be used as a reinforcement agent for polymers like PLA. Torres-Giner *et al.*(105) incorporated alkali-pretreated FFs into PLA via REX and studied the influence of different compatibilization strategies on the resulting composites. A multi-functional epoxy-based styrene-acrylic oligomer (ESAO), a random copolymer of poly(styrene-co-glycidyl methacrylate) (PS-co-GMA), and maleinized linseed oil (MLO) were used as coupling agents. The PLA/FFs composite compatibilized with MLO displayed improved mechanical and thermal properties and the highest ductility (Figure 29) whereas the composites compatibilized with the petroleum-based additives *e.g.* ESAO and PS-co-GMA, showed the highest mechanical resistance and toughness improvement and also the highest thermal stability (Figure 29) (105). Even though, the oil-based compatibilizers bring better mechanical properties to the PLA/FFs composites, the one compatibilized with MLO fully arise from bio-based raw materials (105).



(a) (b)

(c) (d)

Figure 29 (a) Thermogravimetric analysis (TGA) curves with inset zooming the onset of degradation; and (b) first derivate thermogravimetric (DTG) and evolution as a function of temperature of the (c) storage modulus and (d) dynamic damping factor (tan δ) of the poly(lactic acid) (PLA)/flaxseed fiber (FF) pieces compatibilized with (3-glycidyloxypropyl) trimethoxysilane (GPTMS), epoxy-based styrene-acrylic oligomer (ESAO), poly(styrene-co-glycidyl methacrylate) (PS-co-GMA), and maleinized linseed oil (MLO) (105)

Polysaccharides are widely used in both food and pharmaceutical industries. Among them, agar which is synthesized by marine algae and its extraction generate seaweed wastes (SWW) have been incorporated to PLA via REX (106). to produce biocomposites. The addition of MAH and DCP was proven to give composites with improved properties as the additives have a compatibilizing effect.(106) At low content, SWW acts as nucleating agent and led to PLA with the highest crystalline phase (6.5 *vs* 3.2 % for neat PLA) (106). However, the better thermal properties are obtained from the composites with the highest amorphous phase. Moreover, PLA has a decomposition temperature of 346°C, that was shifted to 379°C for composites containing 20 % of SWW and 5 % of compatibilizer (106). SWW could be used as an environmentally friendly alternative to produce biocomposites at lower costs.

The effect of chitosan – a polysaccharide arising from chitin, which is a biopolymer used in the packaging industry – has been used in PLA/poly(butylene succinate)

(PBS) blend (107). Functionalized chitosan (FCH) and DCP were added during the REX process. The obtained nanobiocomposite displayed a UV-blocking effect that may be suitable for packaging applications (107).

Polyhedral oligomeric silsesquioxane (POSS) are organic/inorganic hybrid nanoparticles with [$RSiO_{3/2}$] general formula, where R may be a reactive group that can be varied. Liu *et al.*(108) prepared PLA / aliphatic poly(carbonate)(PPC) / polyethylene glycol-polyhedral oligomeric silsesquioxane (PEG-POSS) composites via REX with $SnOct_2$ as catalyst. PEG-POSS has a hydrophobic structure and hydrophilic side chains (PEG-chains). As PPC is an amorphous polymer, its addition to PLA lead to a decrease in the crystalline fraction of the composite however, the use of PEG-POSS was able to enhance the crystallinity through transesterification reactions between PLA and PPC. PLA water barrier properties were improved by the addition of 20 % PPC and 4 % of PEG-POSS; indeed, the resulting composites displayed a contact angle superior to 90° (108).

II. Ring-opening polymerization of lactide via reactive extrusion

All published works summarized in the previous sections of this review focused on the chemical modification of PLA via REX. In the present section, we will present the research works related to the production and modification of PLA by Ring-Opening Polymerization (ROP) of lactide under reactive extrusion.

The protocol that allowed the production of poly(L-Lactide) (PLA) by ROP of L-Lactide (L-LA) via reactive extrusion (REX), was developed for the first time in 2000 by Jacobsen *et al*.(5,6) The ROP of L-LA was promoted by mixing the monomer with an equimolar quantity of tin(II) octoate ($Sn(Oct)_2$) and triphenylphosphine ($P(Ph)_3$) (Figure 30) (5,6,109). $Sn(Oct)_2$ is a metal-based catalyst which is FDA-approved as a food additive, which allows PLA to be involved in applications in the food packaging industry (8). $P(Ph)_3$ is added to prevent intramolecular transesterification reaction, also called back-biting, a well-known secondary reactions occurring during the ROP of cyclic esters and leading to the formation of cyclic polymers (109). The molar ratio between L-LA and the catalyst may be adjusted depending on the targeted molecular weights of the resulting polymers. In this study, the optimal ratio was found to be 5000 equivalents of monomer *vs.* tin. Reaction conducted at 185°C with a screw speed of

100 rpm lead to a production of PLA with high molecular weight reaching 70 000 g/mol along with nearly quantitative conversion (ca. 98 %) within 7 minutes (4,110–112).

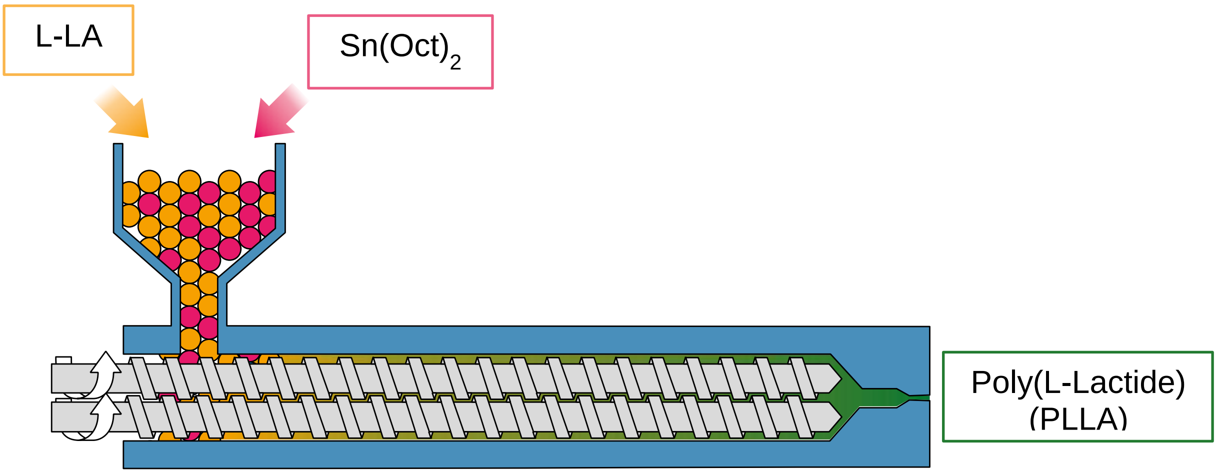


Figure 30 Reactive extrusion process

In a recent study, Fernandez *et al.*(113) work on the synthesis of PLA by reactive extrusion at a pilot plant scale. More precisely, the authors investigated the use of two initiators, 1,12-dodecanediol (DDD) and di(trimethylol propane) (DTMP), to synthesize high molecular weight PLLA. To do so, they used a twin-screw extruder in which L-Lactide was added with Sn(Oct)$_2$, P(Ph)$_3$ and DDD (PLA_DDD) or DTMP (PLA_DTMP).(113) The resulting PLA_DDD and PLA_DTMP reached high average-weight molecular weights (M_w) *i.e.* 183 and 217 kDa with Đ values of 2.44 and 2.36 respectively.

Recently, Abhyankar *et al.*(114) investigated some alternative energy (AE) sources to boost the ROP of lactide during the REX process. Microwaves and ultrasounds were used in an empirical way but also by modelling the reaction. Both microwaves and ultrasounds enhanced the process in terms of molecular weight and monomer conversion in a specific range of temperature (160-180°C). Indeed, working at lower temperature is tricky due to PLA melting point which is about 170°C and the polymer matrix risks to degrade when working at higher temperatures. The REX process assisted with ultrasounds provide polymers with molecular weights increased up to 120 % in comparison to the REX process without ultrasounds (30,100 *vs* 13,700 g/mol). In both cases, a mathematical modelling of the process has been developed. However it still needs to be refined as it predicted molecular weight that were three times higher than the empirical results for some experiments of REX assisted by ultrasounds (115).

REX was also used for the production of PLA macrocycles that display increased glass transition temperature and smaller hydrodynamic volume compared to linear PLA. These macrocycles may find interest in the medical field for drug delivery systems (116). Although performing the ROP of lactide during the REX process is known and well documented in the literature, it remains a challenge especially for the production of PLA-based copolymers. Indeed, during the copolymerization, there is a competition between both monomers (lactide and its comonomer) to access the reactive sites of the catalyst. This competition leads to longer reaction time and sometimes inhibits the copolymerization reaction. Finally, REX may be used to incorporate nanofillers and flame retardant as it allows to polymerize lactide while performing the dispersion of fillers (5,117).

1. PLA arising from other catalysts

In 2015, Bonnet *et al.*(116) reported the production of macrocyclic poly(L-lactide) via reactive extrusion in one step synthesis using $Ln(BH_4)_3(THF)_3$ (Ln = La, Nd, Sm) as catalysts. These macrocycles arise from the intramolecular transesterification reactions that occur during the ring-opening polymerization. It is noteworthy that they can be produced by operating at lower temperature (130°C) than the usual ROP of L-lactide via REX (usually at 185°C). Cyclic polyesters are polymers of high interest as they have potential applications in the biomedical field. The authors pointed out that their metal-based catalysts involved in this work displayed low toxicities which confirms that PLA macrocycles are appropriate for such applications (116). It was further shown that linear and macrocyclic PLA of same molecular weights exhibit slight differences in terms of crystallinity (59 *vs* 50 %) or glass transition temperature (53 *vs* 56°C) (118). Moreover, the melting temperature of macrocyclic PLA was found to be lower than its linear analog (163 *vs* 171 °C) (118). The tensile tests also show differences that were attributed to the constrained network implied by the macrocyclic topology. Indeed at 70°C PLA displays a higher deformation capacity than macrocyclic PLA which was attributed to the possible macrocycles entangled (118).

The same group used a titanium oxo-cluster to synthesize a hybrid PLA via REX (119). The oxo-cluster acted both as a catalyst and as crosslinking agent allowing to obtain

PLA with M_n of about 58 000 g.mol^{-1} (119). The EPMA (electron probe microanalyser) analysis highlighted a good dispersion of the filler into the polymer matrix. Moreover, the hybrid PLA displayed a superior dimensional stability than the commercial one. Indeed, the dimensional stability tests under heat showed an almost unchanged shape for hybrid PLA after 10 h at 150°C, whereas the commercial PLA sample was distorted (119).

Raquez *et al.*(120) developed a greener magnesium-based catalyst (*i.e.* magnesium (II) N-heterocyclic carbene) in order to allow the continuous polymerization of lactide via REX. They proved that their new catalyst, used in a microcompounder, was able to provided PLA with high molecular weight (47,500 g/mol), low polydispersity index, no epimerization and a conversion of lactide of 80% at a temperature of 170°C (120). Reactions conducted at 190°C led to lower molecular weight PLA with high dispersity (above 2) as long as epimerization rates up to 15%. The authors believe that magnesium (II) N-heterocyclic carbene is a promising catalyst in order to improve the eco-friendliness of the continuous synthesis of PLA via reactive extrusion (120).

2. Copolymers

As a biodegradable and biocompatible polymer PLA is considered as a material of huge interest for the medical and pharmaceutical fields.(12) Régibeau *et al.*(11) presented in 2020 a synthesis of a medical grade of poly(D,L-lactide-co-glycolide) (PLGA) (Figure 31) via the ROP of lactide and glycolide during the REX process. The optimization of both screw and barrel designs allowed them to get 95 % conversion within 10 min, affording polymers with molecular weights up to 50 000 g/mol (11).

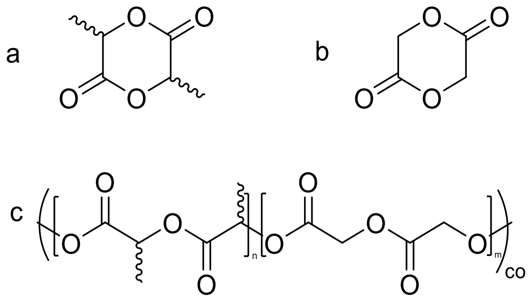


Figure 31 Chemical structure of D,L-lactide (a), glycolide (b) and PLGA (c) (11)

Another cyclic polyester that is commonly polymerized by ROP promoted by $Sn(Oct)_2$ is ε-caprolactone (ε-CL) (4). Thus, poly(L-lactide-co-ε-caprolactone) can also be produced by REX. The process is described by Nishida *et al.*(121) who designed a three steps process including two REX separated by a mixing step . L-LA and Sn(Oct)$_2$ were extruded into a mixing hopper where the mixture was stirred with ε-CL prior to be extruded. The resulting random copolymer displayed mechanical properties that were lower than those of neat PLA *e.g.* the tensile strength was reduced of 50 to 20 MPa and the tensile elastic modulus dropped from 2500 MPa to 1500 MPa. In fact, this decrease was inversely proportional to the ε-CL of the copolymer (121). These poly(L-lactide-co-ε-caprolactone) copolymers with high ε-CL content can find their utility in the medical or pharmaceutical field, as the biodegradability can be modulated with the CL content and the type of copolymer formed (block, gradient or statistical).

A block copolymer PLA-b-PE was synthesized by Núñez et al.(55). To do so, an intermediate product (PE-OH) was synthesized by coordination-insertion polymerization using the zirconocene Cp$_2$ZrCl$_2$ at 50°C in toluene. Then, the block copolymer was obtained via ROP by reacting PE-OH with L-lactide and Sn(Oct)$_2$. The resulting copolymer was used to compatibilize a blend of PLA and PE.

Another type of block copolymer that is PLA-co-poly(propylene adipate) (PPAd) was developed by Terzopoulou *et al.*(122) in order to tune the degradation properties of PLA. After the polymerization of L-lactide with PPAd oligomers by REX at 180°C during 20 minutes, the obtained PLA / PPAd copolymers reached number average molecular weights up to 63,000 g/mol however the PPAd was inserted into the copolymer, the lower the molecular weight was (122). Indeed, PPAd acted as a macroinitiator which lead to an increased number of growing chains resulting in lower molecular weight. Moreover, the incorporation of PPAD into the PLA backbone contributed to increase the hydrolysis rate with and without enzyme of the copolymer in comparison with neat PLA (Figure 32).

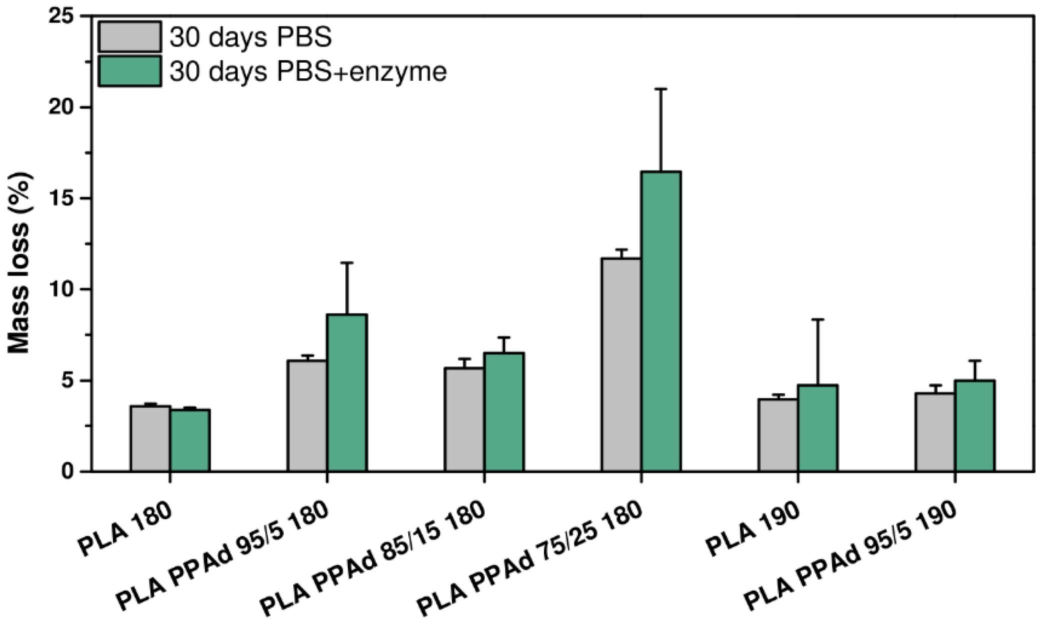


Figure 32 Effect of the presence of enzymes in the hydrolysis of the samples for 30 days(122)

3. Nanocomposites and complexed PLA

The incorporation of nanofillers *e.g.* silica, layered silicates, POSS and graphite (117), to the polymer matrix during the ROP of lactide via REX is often used to enhance PLA properties in terms of crystallinity, stiffness or thermal stability as described in the following papers (117,123).

The addition of graphite nanoplatelets (GNP) during the ROP of L-LA via REX was performed by Fina *et al.*(117) In particular the effect of the addition of molecules containing a pyrene end group and a poly(D-lactide) (PDLA) chain (Pyr-D) was studied (Figure 33). In the presence of PDLA, the L-lactic acid segment of PLLA will strongly interact with the D-lactic acid segments resulting in the formation of stereocomplexes (124,125). The PLA/GNP nanocomposites were found to be both thermally and electrically conductive. Moreover, the presence of stereo complexed regions increased the thermal conductivity of the PLA-based nanocomposites (117).

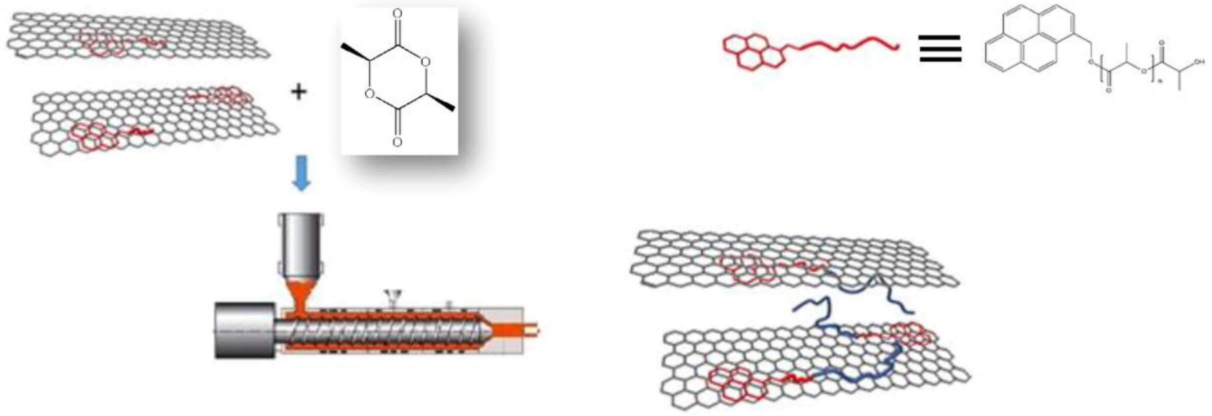


Figure 33 Scheme of the nanocomposites preparation procedure(117)

Zhen *et al.*(123) synthesized aminated benzoic acid intercalated layered double hydroxides (AB-LDH). The latter was feed with L-LA and zinc lactate as the catalyst in an extruder to obtain PLA / AB-LDH nanocomposites. Thanks to an orthogonal design of experiment, they determined the optimum process conditions which were 2 wt % of catalyst, 0.3 wt % of AB-LDH, a polymerization temperature of 170°C and a screw speed of 20 rpm. AB-LDH act as nucleating agent which lead to an increase in PLA nucleation density and crystallinity. Moreover, studies on the thermal decomposition kinetics shows that, compared to neat PLA, the composite's thermal decomposition activation energy is increased (34 kJ/mol *vs* 22 kJ/mol for neat PLA) (123) and the thermal stability of PLA is improved. Indeed, the decomposition temperature of the nanocomposite lies between 250°C and 300°C depending on the heating rates whereas it is between 240°C and 280°C for neat PLA (123).

The addition of organically modified clay during the ROP of L-LA via REX was performed by Nishida *et al.*(126). They observed that the obtained PLA / clay nanocomposites had an intercalative morphology that affected the NMR parameters: T_1C (overall carbon relaxation time) and T_1H (overall proton relaxation time). Indeed, the nanocomposite had a different behavior resulting in decreased T_1H values above room temperature (126). T_1H can be used as an indicator of the nanofiller dispersion into the polymer matrix (127). Indeed, the paramagnetic Fe^{3+} from the clay acts as relaxation sinks for proton leading to shortened relaxation time (127). Therefore, using these data, calculations can be done to characterize the clay dispersion (127). Moreover, the organoclay accelerate the relaxation time of ^{13}C nuclei especially for temperatures above the T_c (crystallization temperature) (126). The TGA results also showed that the presence of montmorillonite increased the decomposition temperature (T_{dec}) compared to neat PLA (278°C *vs* 260°C) (126).

Salimi *et al.*(128) mixed starch (St) with LA and montmorillonite (MMT), an organoclay. Their goal was to enhance the adhesion between both phases of the composite leading to a potential candidate for petroleum-based plastics substitution. The first step consisted in mechanical stirring followed by reactive extrusion in order to increase the degree of grafting (Figure 34). The obtained St-g-PLA copolymers and St-g-PLA / MMT nanocomposites were designed to produce films. Compared to St-g-PLA, the nanocomposite displays higher thermal stability as proven by the TGA analysis. The thermograms appeared to be shifted from 10-20°C to the right (128). Moreover, the addition of 5 % of MMT enhanced St-g-PLA mechanical properties in terms of elongation at break (5.2 *vs* 3.6 %), tensile strength (82.4 *vs* 52.4 N/mm^2) and Young's modulus (531 *vs* 140 N/mm^2) (128).

Li *et al.*(129) prepared PLA-ϒ-cyclodextrin inclusion complexes from multi-branched PLA (PLA-IC-PLA) starting from L-lactide. The thermal analysis (TGA, DSC) showed that PLA-IC-PLA displayed a lower T_g as well as a 3 % higher crystallinity whereas the TG curves showed similar profiles (129). Moreover, the branching brought better mechanical properties to PLA-IC-PLA with a slightly higher elongation at break and an improved impact strength (7 *vs* 5 kJ/m^2). PLA-IC-PLA has an enhanced hydrophilicity compared to neat PLA. This branched complexed polymer may have a potential use in biomedical materials (129).

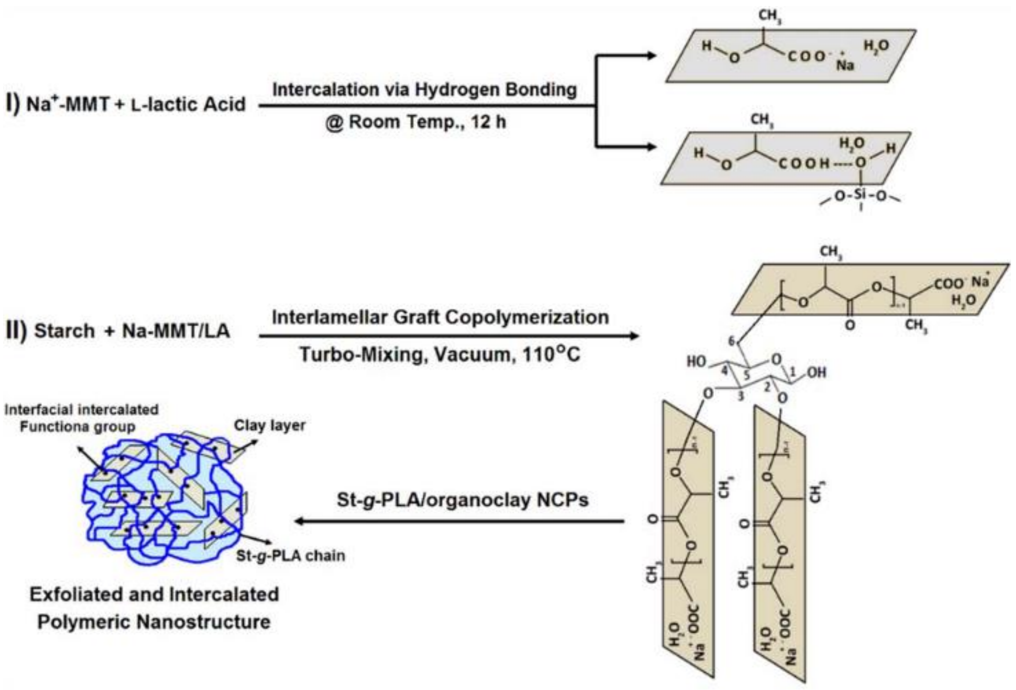


Figure 34 Schematic representation of the St-g-PLA/organoclay nanocomposite synthesis via a shear mixer and reactive extrusion(128)

4. Flame Retardancy

The flame retardancy of PLA is a challenging subject, however PLA has to be flame-retarded for being involved in long-lasting applications such as in automotive, aircraft or electronic fields.

Another example of using carbon as nanofiller in PLA nanocomposite is the work of Bourbigot *et al.*(110) The REX process of PLA / multi-wall carbon nanotubes (MWNT) (1 wt% of fillers) provided materials with an acceptable dispersion, *i.e.* the dispersion of MWNT particles in the polymer matrix was satisfactory and good enough to provide fire retardancy. PLA nanocomposites had an enhanced thermal stability compared to neat PLA. Indeed, the fire tests that were conducted on the resulting polymer also showed an enhanced flame retardancy that was determined by mass loss calorimetry. However, it could have been higher with a better dispersion of the nanofillers in the polymer matrix (110). The influence of MWNT on the thermal stability of PLA was also assessed by Gallos *et al.*(112) in 2014 where nanocomposites were produced by REX during the polymerization poly-L,D-lactide stereocomplexes. An improvement of the thermal stability was highlighted by TGA analysis. The first decomposition step of PDLLA-MWNT nanocomposite occurs at 209°C *vs* 170°C for PDLLA. However this improvement was reduced in the presence of α-tropolone, which is the component used to deactivate the catalyst ($Sn(Oct)_2$) (112). Indeed, the first decomposition step of PDLLA-MWNT nanocomposite containing α-tropolone occurs at 193°C. Moreover, the formation of a char layer was observed during fire test (mass loss calorimetry experiment). The role of this layer is to reduce the volatile escaping to the flame and acts as a thermal insulator during a certain period of time (110).

Flame retarded materials can also be obtained by the addition of intumescent additives. Upon heating, an insulative, expanded charred coating will develop at the surface of the polymer and provide low flammability (111). An intumescent stereocomplexed PLA was successfully obtained when a combination of ammonium polyphosphate (APP), melamine and organoclay were mixed with L-LA, D-LA and $Sn(Oct)_2$ / PPh_3 (1:1 mol%) in a twin-screw extruder (111). More precisely, 20 g of L-LA were first added with the $Sn(Oct)_2$ / PPh_3 mixture and the polymerization was followed with the evolution of the torque. When it reached a plateau, half of the synthesized PLLA was removed from the extruder and 10 g of D-LA with the $Sn(Oct)_2$ / PPh_3 mixture were added. Finally, α-tropolone was used to deactivate the catalyst and both APP, melamine and organoclay were added (111). This provided materials with significantly improved fire properties compared to neat PLA (111). APP and melamine are conventional flame retardants which, with nanoclay, reacts upon heating and lead to the formation of a char. The mass loss calorimeter results shown a significant reduction of the pHRR (peak heat release rate) of flame retarded PDLLA (50 *vs* 250 kW/m^2 for PDLLA) (111).

However, the above-mentioned methods present some drawbacks that are the potential leaching and migration of the additives. Thus, a solution to these problem is the incorporation of fire-retardant (FR) moieties directly in the PLA backbone which was investigated by Mincheva's *et al.*(130). A three-steps process (Figure 35) was developed including the synthesis of a [9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide]-based initiator (DOPO-diamine) that was used during the ROP of L-LA in bulk. DOPO-PLA was coupled with hexamethylene diisocyanate (HDI) leading to the formation of DOPO-PLA-PU which were mixed with commercial PLA. Compared to commercial PLA, DOPO-PLA-PU exhibited enhanced fire properties at the cone calorimeter and UL-94 tests. The pHRR (peak heat release rate) was reduced by 35 % and the THR (total heat release) was reduced by 36 % compared to neat PLA (130).

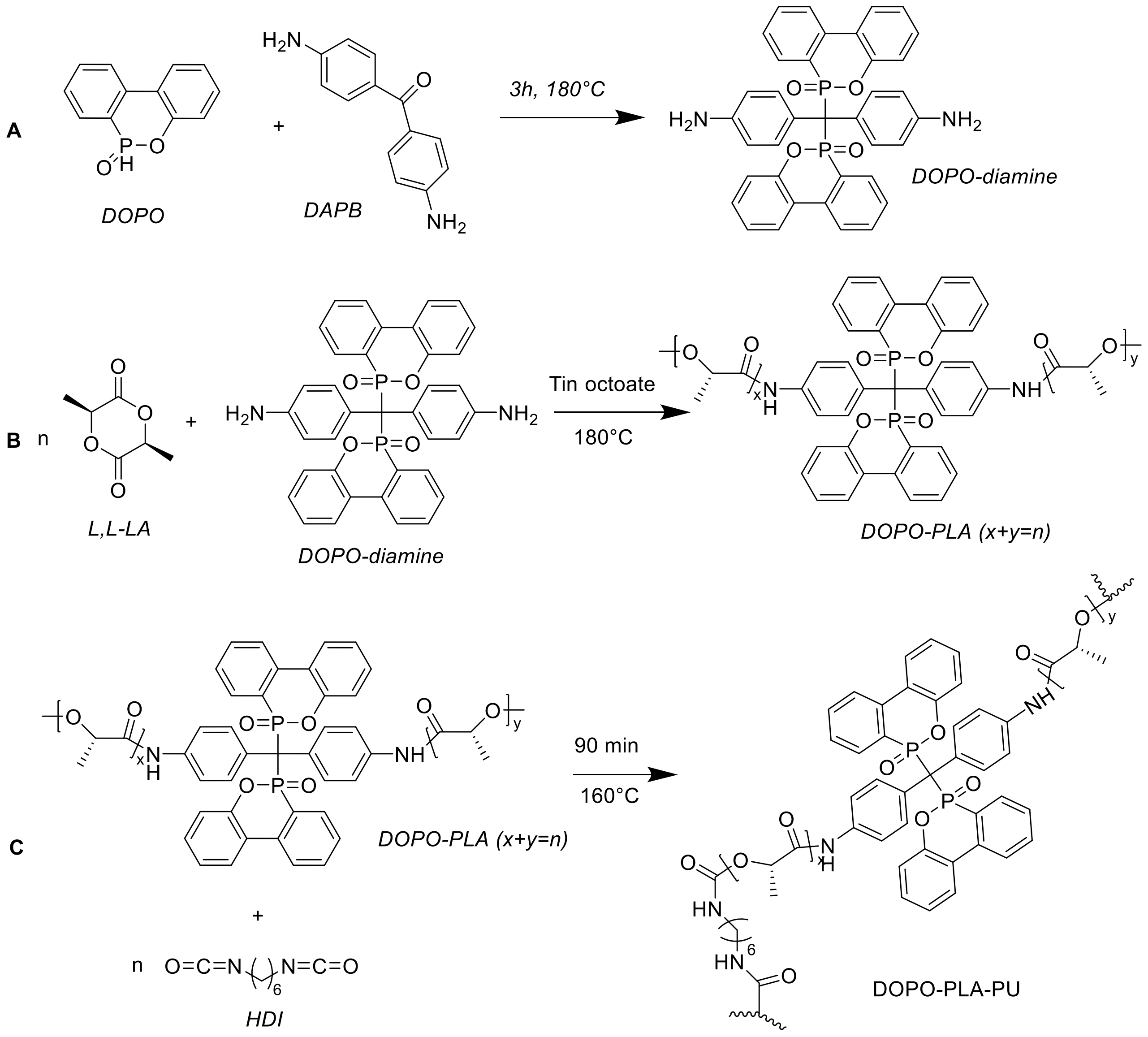


Figure 35 Three-step synthetic pathway to 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-poly(lactic acid) (PLA) PUs: (A) Synthesis of DOPO-diamine; (B) DOPO-initiated bulk ring-opening polymerization (ROP) of L,L-lactide (L,L-LA); (C) chain coupling reaction (130)

Conclusion

Many pathways have been developed to synthesize PLA with improved thermo-mechanical properties. One of the most common strategy involves the blending of commercial PLA with other polymers and compatibilizing agents. The development of PLA-based composites is also a well-studied route. It usually involves peroxides to create radicals allowing the grafting of molecules onto PLA backbone. Most of the studies exploring these strategies explore the use of petroleum-based polymers or non-sustainable additives. However, one of the challenges in the chemical modification of PLA is to improve its mechanical properties while retaining its biodegradability. Therefore, sustainable modification routes of PLA have focused on the use of biosourced additives such as functionalized vegetable oil or food industry byproducts flour *e.g.* walnut shell, almond shell, orange peel. However, complementary studies assessing the sustainability of the obtained PLA-based blends or composites would be required. The chemical modification of PLA starting from L-lactide allows the insertion of a comonomer or moiety into the PLA backbone which can prevent potential leaching or migration of the active functionality. This route may offer a wider range of possibilities for the modification of PLA but is highly challenging. This route offers possibilities to design specific comonomer to give a targeted property to resulting PLA. The thermal, mechanical and rheological properties enhancement of PLA can be performed with the addition of additives during the reactive extrusion process, opening perspectives for the incorporation of additives, and in particular flame retardants, the fireproofing of PLA still being a challenge. However, the number of steps needed may prevent it from being compatible with an industrial process. A new area of research would be to design a single-step reactive extrusion process that will allow the incorporation of functional moieties in the PLLA backbone during the ring-opening polymerization of L-LA. It could be, for example, used to develop a flame retardant biopolymer, which would therefore be used for long lasting applications in the automotive industry. In both fields *i.e.* modification of commercial PLA and modification of PLA during its synthesis, the sustainability of the modified PLA should be targeted and assessed. Indeed, neat PLA is considered as a green alternative to petroleum-based polymer since it is compostable. Therefore, modified PLA should keep this feature. To do so, new bio-based and compostable additives should be designed. Moreover, in this pandemic context, functionalization of PLA with antibacterial groups would enlarge its range of use *e.g.* as a virucidal or bactericidal sustainable coating in the medical field.

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