

# Compounding and processing of biodegradable materials based on PLA for packaging applications: In greening the 21st century materials world.

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**Abstract.** Poly(lactic acid) is a well known polymer for more than 20 years in the biomedical fields applications. Today, according to rising prices of oil and massive consumption of fossil resource, this biodegradable aliphatic polyester is on the way to be a wide used commodity polymer. Moreover PLA is as a “green plastic” because it is synthesized from annually renewable resources. In many ways similar to poly(ethylene terephthalate) such as rigidity, transparency, crystallization kinetics and food contact ability, it fulfills the packaging industry requirements for most of the rigid objects. But for applications like hot food packages, soft films and stretch blow bottles for example some properties of PLA have to be improved like heat deflection temperature (HDT), impact stiffness and gas barrier properties. There are many ways reported in literature today to improve these properties. In order to compare it with other well known polymers, figure 1 represents thermal properties of PLA and these polymers. The aim of the work deals to identify actual weaknesses of commercial grades of PLA. Secondly, to present pertinent ways to improve PLA's properties have been identified according to chosen process and final properties wished. This study is composed of three main items. In a first time, a bibliographical study is necessary to identify the different ways to improve PLA's properties used by researchers and industrials in literature. The most significant ways will be describe here. Then PLA compound (PLA with additives or PLA copolymers for examples) will be synthesized in conditions closed to industrial conditions studying crystallisation kinetic and rheological properties. In this step thermal, physico-chemical and mechanical properties of products synthesized will be characterized. At the end of this study the best ways of improving PLA's behavior will be presented and described [1].

**Key words:** biopolymers, biodegradable, compounding, rheology, PLA, crystallization,

## 1. State of the art

Lactic acid, the basic block to synthesize PLA, was isolated for the first time in 1780 by a Swedish chemist Scheele and first commercially available in 1881. Lactic acid is used in many processed foods as a bacterial inhibitor or acidic flavoring agent for example. The common way to produce industrial lactic acid is by bacterial fermentation of agricultural raw materials such as corn or potato starch, cane or beet sugar but also waste materials from agricultural production. Then PLA can be polymerized by different ways: polymerization of lactic acid by polycondensation or by dimerization of lactic acid to obtain lactide and then ring opening polymerization to obtain polylactide [2-5]. This method is able to produce high molecular weights PLA at an industrial scale.

The farthest developments of using PLA in packaging industry are for food, fruits, vegetables and snacks, as well as catering products for cold beverages and meals. Industrial and commercial grades of PLA are available on the market [13-17]. Today Cargill Dow's Natureworks™ is the leader of PLA production with a capacity of production (in 2007) of 140 000 tons/year. Natureworks™ PLA have a good clarity and glossy, heat-sealing ability, oil and fat stability, better torsion strength than cellophane (+25%), taste and flavour barrier, good ability to be printed on, enough stiffness to produce hard package and blow moulding products, crease resistance, workability on conventional equipments and of course it is environmentally friendly (lower fossil raw materials and energy consumption, smaller emissions of greenhouse gases, renewable raw materials and compostable). So this commercial PLA according to its properties can be used in a wide range of applications. But PLA have weakness. A low heat deflection temperature (about 50°C) restrains PLA to low temperatures applications. PLA has also insufficient gases barrier properties regard to PET and have a weak impact resistance. These three major weaknesses of PLA have to be improved in order to use PLA in a wide range of packaging applications: microwavable pack, bottles and films with barrier properties [13-15].

There are many ways describe in the literature to improve these properties of PLA. First of them is to improve crystallisation kinetic and crystalline properties of PLA. This can be done by using, for example, nucleating agents or plasticizers. Crystallinity is also a way to improve mechanical properties of PLA under temperature. Impact resistance should be improved using plasticizers. Nanostructured PLA and multiphase polymers based on PLA are also reported in literature for increasing PLA's mechanical properties and helping biodegradability [16-25].

### 1.1. Modification of crystalline property of PLA

#### 1.1.1. Introduction

It is reported in literature that the maximum PLA crystalline content is about 35% to 45% but crystallization kinetic of neat PLA is very slow and thus processability of crystalline PLA would be difficult for process like extrusion or injection [3-6]. This is one of the main reasons to improve crystallinity and crystallization kinetics of PLA. The other one is to improve behaviour of PLA under temperature because above its glass transition temperature (about 60°C) only the crystalline PLA phase can confer useful mechanical properties. There are three major ways to improve crystalline properties of PLA: the use of nucleants to lower the free surface energy and initiate crystallization, the use of plasticizers to increase chain polymer mobility and so helping crystallization and playing with process parameters and moulding conditions to reach the best level of Crystallinity [6-8].

### 1.1.2. Semi-crystalline PLA – stereocomplexed PLA

Lactic acid exists in two optical enantiomers: L-lactic and D-lactic. Ring opening polymerization is today the common industrial way to produce poly(lactic acid) with high molecular weight. L-lactide and D-lactide are dimers of two L-lactic (or D-lactic) acid. Mesolactic is a dimer of one L-lactic and one D-lactic. PLLA: poly(L-lactic acid) and PDLA: poly(D-lactic acid) are the polymers associated with these two morphologies. Fermentation process of corn tends to favor production of L-lactic [1,4,6]. So commercially available poly(lactic acid) is a mixture of L-lactic and D-lactic with a major contents of L enantiomers [28-32]. It is reported that an amorphous commercial grade of PLA have a ratio L:D of 80:20 to 98:2 (molar ratio) and a semi-crystalline commercial grade a L:D ratio of 98.4:1.6 to 98:2. When PLLA and PDLA are blended they form a stereocomplex that can act as a nucleation site for PLLA when cooled at a temperature below  $T_m$  of PLLA. As a conclusion the stereochemistry of PLA is complex because of its chiral nature. Control of the ratio of L to D monomer content is an important molecular feature for PLA.

### 1.1.3. Nucleants and plasticizers

A large amount of nucleants for PLA was reported by researchers. First of them, talc, is a well known filler widely used with polymers. Literature reports [1-3] that talc is also a good nucleating agent for PLA. With addition of talc it is possible to reach the 40% of crystalline phase in PLA. But this result was obtained in specific conditions with a slow cooling rate not suitable for industrial production (cooling rate are greater than  $10^\circ\text{C}/\text{min}$  in injection moulding for example). For high cooling rate, plasticizer combine with talc increased the crystalline kinetics of moulded PLA but mould temperature has to be in the  $70\text{-}100^\circ\text{C}$  range. The plasticizer showing the best results in literature was poly(ethylene-glycol) PEG added at about 10% wt. It was also described that plasticizers of low molecular weights are better than high molecular weights PEG, because they are more able to migrate from the intraspherulitic amorphous layer to the front of growing spherulite helping them to grow easily. But for application such as food packaging, ability of polymer migration is not suitable. As a result of blending PLA with PEG, glass transition was lowered. The solubility limit of PEG in PLA occurs when melt glass transition temperature stopped to decrease. In the case of amorphous PLA, it is reported that transition from brittle to ductile occurs when  $T_g$  is shifted to  $35^\circ\text{C}$ . So the use of plasticizers will increase elongation at break, and lowering tensile modulus and brittleness of blend [13,20]. As a conclusion the use of plasticizers in PLA can modify properties of both amorphous and semi-crystalline PLA. Other efficient plasticizers for PLA reported in literature are citrate esters or triacetine. Other nucleating agents suitable for PLA according to literature are aliphatic amide compound. For example ethylenebis (12-hydroxysterylamide) called EBHSA [1]. Results show a greater nucleation density with smaller spherulites than neat PLA. One other organic compound family was found as PLA's nucleating agent in literature: hydrazide compound. An interesting study has compared efficiency of PLA mixed with hydrazide compound (1% wt.) or aliphatic amide compound and talc (1% + 1% wt) in injection moulding conditions. The properties of injected compound were quite impressive. HDT (Heat Deflection Temperature) and impact resistance were increased more than twice of neat PLA. But on the processability point of view injection time cycle was not industrially viable for aliphatic amide compound and talc (injection cycle was about 7 min). For hydrazide compound injection cycle was reduced to less than 3 min. As reference polypropylene injection cycle is about 1.5 min. EBHSA and talc are readily available products but hydrazide compounds have been synthesized at laboratory scale [21-25].

### 1.1.4. Processing parameters

Literature is quite poor about the influence of processes parameters on PLA crystallization [21]. DSC analysis can be useful to predict PLA behaviour when processing. The literature showed that annealing material above its glass transition temperature ( $80^\circ\text{C}$ ) increased polymer chain relaxation (for both

amorphous and semi-crystalline PLA) and crystallinity (in the case of a semi-crystalline PLA). One can remark that annealing material within an industrial framework of producing PLA may be sometimes difficult to realize. Sakai et al. in their study processed PLA (with nucleating agents) with a mould temperature of 110°C to enhance crystallization. The process parameters and their influence when transforming PLA will be studied during the experimental part of this report.

### ***Effect of Annealing and Orientation on Microstructures and Mechanical Properties of Polylactic Acid***

Previous studies have shown that there are two kinds of crystal structure in PLA, depending on the formation conditions: an  $\alpha$  form (pseudo-orthorhombic, pseudo-hexagonal, or orthorhombic) and a  $\beta$  form (orthorhombic or trigonal). Hoogsteen et al. [28] investigated the effect of solution spinning on the microstructure of PLA, and found that the b/a ratio increased with increasing draw ratio. Similar results were also reported by Sawal et al. [30]. Kocuturk et al. [31] studied the development of crystal structure and orientation during uniaxial stretching of linear and branched PLA films using an Instron tensile tester with a temperature controlled environmental chamber in the temperature range of 65–85°C. It was found that stretching the materials above their  $T_g$  produced rapid orientation in the amorphous state, and beyond a critical level, very sharp and highly oriented b-crystalline formed chains with 3/1 helices. When stretching at or below  $T_g$ , the films were found to revert to a highly oriented amorphous state through the destruction of the crystalline domains.

## 1.2. Other ways of modification of PLA

In this second part of this bibliographical study, an overview of other ways of modifying PLA will be given. One of the promising ways of these modifications is nanostructuring of PLA. Nanoclays and core-shell rubbers are the most related nanostructurants for PLA in literature. Chain extension mechanism has also been identified to modify PLA. With chain extenders average molecular weights of polymers should be increased and thus should increase physical and mechanical behaviour of the material. Last way of PLA's modification that will be discussed in this part is PLA blending with other biopolymers or polymers. A lot of blends could be considered, but just a few examples will be described in this study.

### 1.2.1. Composites based on PLA.

One promising way for improving that behaviour of PLA is its nanostructuring [11-12]. Nanoclay and Core-Shell rubbers, according to literature, are the most promising materials for that nanostructuring [5,20].

*a) Core-Shell rubbers generally consist of a crosslinked elastomeric core of controlled composition and size produced by the emulsion polymerization process with a thermoplastic shell encapsulating core (range of size 50-500 nm). Surface of core-shell can also be grafted (or not) in order to enhance compatibility with material. These core-shell are generally use as an impact modifier (for plastics) improving impact resistance of PLA. Parameters that influence efficiency of these core-shells are: size of particles and the quality of their dispersion in the polymer matrix, rubber glass transition temperature and the adhesion to the polymer matrix. This adhesion and property improvements depend on the surface chemistry of shells. Literature reports additions of about 5% to 10% wt of core-shells in PLA matrix. Efficient core-shells for PLA related in literature have a polybutylacrylate core with a polymethylmethacrylate shell. Recently Rohm & Haas presented its first commercially available acrylic based Core-Shell for impact modification of PLA known under Paraloid™ BPM 500. Rohm & Haas presented quite impressive results in terms of improvement of impact resistance. Moreover this additive keeps the transparency properties of PLA. Rohm & Haas claimed that addition of 7.5% wt of Paraloid™ BPM 500 improve dart drop impact resistance of*

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PLA more than 5 times than with neat PLA . Other suppliers like Dupont™, Arkema and BASF developed their own impact modifiers for PLA.

b) Other nanostructurants useful for PLA found in literature are nanoclays. Montmorillonite (MMT) is the most related clay in literature for improving properties of PLA. These particles are plate-shaped with an average thickness of approximately 1 nm. Length varies from several tens to several hundred of nanometres. Surface of platelets is generally modified with surfactants to provide miscibility with the polymer and allowing complete dispersion. Moreover MMT is economical, naturally abundant and environmentally friendly. Clay contents in PLA matrix related in literature are up to 10% wt. The most important issue to withdraw is a good dispersion of clay in the polymer matrix. The hydrophilic nature of PLA confers it more ability to be compatible with hydrophilic surfactants on clay. The use of compatibilizers like elastomeric ethylene copolymers has been reported to enhance the degree of exfoliation of the organoclay. As properties improvement, it was reported that MMT improve the heat deflection temperature (HDT) of material (76°C for neat PLA and 110°C for PLA with 7% wt of MMT under à 0.98 MPa load), gas barrier properties (clay creates a 'labyrinth' that retard the progress of gas molecules through the matrix resin) and help biodegrading of material. There was also reported that clay can acts also as nucleant for PLA [11-12]. Southern Clay Products produces commercial grades of MMT with different surface treatments. Cloisite® and Nanofil® are these products name. Cloisite® 30B was reported to be the more suitable clay for PLA according to its hydrophilic surface.

c) Core-Shell and Nanoclays

Tonggnian et al. [20] also reports the synthesis of PLA composites using MMT nanoclays and core-shell rubbers. It was reported that the use of core-shell rubbers enhanced the degree of exfoliation of MMT.

### 1.2.2. Chain extension or crosslinking of PLA

Another way to improve mechanical properties of PLA reported in literature is chain extension [4,7]. Chain extension increases molecular weights of polymer, strength of melt (acting like a crosslinker) and also can be use a reactive compatibilizer in blends [26-27]. Moreover a study show that branched PLA are more able to cold crystallize. When compounding polyesters molecular weights are subjected to degradation. It is reported that this degradation could be fast when processing at high temperature or shear rate. That can cause a loss of physical and mechanical properties of polymer. First related chain extension experiments of PLA were done with isocyanate compound. This molecule is known to be toxic and highly volatile so there are few interests for using it within the framework of this study. With such a technique, researchers increased PLA's modulus, elongation at break and glass transition temperature.

Another chain extenders related in literature is DGEBA-based epoxy resins (Zhou et al. [7]). In this study, a modified PLA (dicarboxylated obtained with succinic anhydride) was blended with DGEBA with the help of a catalyst tetrabutylammonium bromide (TBAB). Chain extension was performed in a rotavapor rotating at 150 rpm under a 100 Pa pressure and at 150°C. Best results were obtained for a mol ratio of dicarboxylated PLLA and DGEBA of 1:1 (85% PLLA, 14% DGEBA and 1% TBAB). Results presents a molecular weight improve from 10,000 to about 87,000 g/mol without gel content. In this study chain extension was mainly linear. Evidence of reaction was done using FTIR analysis.

BASF Joncryn® is a commercially available chain extender for PET and PLA that uses non linear chain extension. This product is an epoxy-functional styrene-acrylic based or styrene-free acrylic based reactive polymers. According to the supplier, it is composed of low and high epoxy functionalities that allow

molecular weight modifications in a much larger processing window. There are two advantages with BASF Joncryl®: it can be purchased as a solid (useful for reactive extrusion) and it has the food contact agreement [1]. Results showed by supplier are quite impressive improving molecular weight from 125,000 to 425,000 g/mol within the addition of 1.7% of this commercial product (process parameter : reaction time 6 min at 220°C with grade 6300 of PLA from Natureworks™). Moreover this chain extension mechanism is patented by Natureworks® LLC. To perform chain extension of PLA, molecules containing epoxy functions seems to be the most promising way.

### 1.2.3. Multiphase materials and copolymers based on PLA

Other way of improving properties of PLA is to blend it with others molecules. Literature is very rich about blending PLA with other polymers or biopolymers. Most related studies are about blends of PLA with thermoplastic starch and/or poly( $\epsilon$ -caprolactone). Some studies also report synthesis of PLA based copolymers. At last the great amount of polymers and materials existing today in the market can led to think and search about new polymers and blends based on PLA.

#### 1.2.3.1. PLA compounds with thermoplastic starch.

Thermoplastic starch (TPS) is a low cost biopolymer product from annually resources. Drawbacks of this polymer are its poor mechanical properties and high sensitivity to moisture. Starch is composed of two polysaccharides: amylose and amylopectin. Amylose is generally the minor component in starch. Amount of amylose and amylopectin in starch depend on starch source. Amylose is a linear macromolecule and amylopectin is a branched macromolecule. In order to be processable, starch has to be plasticized and gelatinized (that is to say making disappeared crystalline structure of starch at 70-90°C in presence of water or glycerol acting as plasticizer). Blending PLA and TPS without compatibilizer or initial treatment leads to a material with very poor properties. Grafted PLA with maleic anhydride in a single screw extruder can be prepared (Sarazin et al. [4]). Then PLA modified was blended with TPS in another single screw extruder. For glycerol content in TPS of 36% at least, TPS-PLA blends showed improved ductility and elongation at break between 100 and 200%. Researchers explain this enhancement by a better homogeneity of the blend with grafted PLA than blend with neat PLA. In another study dioctyl maleate was found to be efficient compatibilizer and plasticizer for PLA + TPS blend but results are less impressive.

In another study Sarazin et al. blended PLA or PLA+PCL with TPS without any treatment. Results show enhancement of properties of PLA especially elongation at break and impact resistance. But improvement of elongation at break is not as important as in the previous described study. Nevertheless it appears that the presence of PCL at about 10% wt. improve impact resistance (and ductility) compared to neat PLA by three. This study confirms the need of a TPS with at least 36% of glycerol.

#### 1.2.3.2. Copolymers based on PLA

PLA-based copolymers found in literature are principally intended to the field of medical applications. But these experiments may have some interest within the frame of this study to find new ways of development for PLA. Cohn et al. report synthesis of PLA-PCL or PEO-PLA block copolymers in a two step process. First step is the synthesis of PLA-PEO-PLA or PLA-PCL-PLA triblocks copolymers by a solvent way. Second step consists of crosslinking these blocks with the help of hexamethylene diisocyanate (HDI). Results show impressive elongation at break for synthesized materials (600% for PLA-PCL copolymer and

1000% for PLA-PEO copolymers). Solvent way is not compatible with industrial process for packaging industry but crosslinking of PLA, as described in part 1-2-2, is possible in reactive extrusion.

### 1.2.3.3. Other blend based on PLA

The second most important natural polymer in the world is chitin. Main sources are marine crustaceans like crabs or shrimps. Chitosan is a derivative of chitin when its rate of deacetylation reaches 50%. Chitosan is a semicrystalline polymer. Hydrophilic nature of chitosan may affect its stability. Most applications of chitosan are found in medical area according to its biocompatibility. Moreover chitosan possess barrier, anti-microbial and fungicidal properties. So in the field of packaging application, blending chitosan with PLA may be a promising way for bioactive film production. Nevertheless most related synthesis of PLA-chitosan blend is made by film casting. This way of synthesis is not conceivable for an industrial scale process. When blended together, PLA did not react with chitosan. One study of Correlo et al. [5] related blending of PLA with chitosan by melt processing. Authors synthesized a 50:50 PLA chitosan blend in a twin screw corotating extruder (TSE). Unfortunately, little information is given about chitosan used and its preparation before blending with PLA. Thermal profile and rotating speed in TSE are given. Results showed that chitosan acts as a nucleating agent for PLA initiating cold crystallisation at 90°C (100-110°C for neat PLA). Tensile strength and elongation at break decreased compare to neat PLA. But these are not searched properties for such blend. Most important are barrier and fungicidal that seems to be carried with chitosan. Related article did not analyse barrier properties of synthesized material. Finally the literature reported that the use of MDI as compatibilizer enhance interfacial adhesion between PLA and chitosan and PLA crystallinity without leaving free isocyanates according to MDI reaction with water. To conclude, according to the amount of commercial polymers available on the market, one can imagine that a large amount of blend based on PLA that should be synthesized in the next few years. Actual impressive growth of biopolymer market leads researcher and industrial to develop more and more new products

In this bibliographical study, most promising way of enhancing PLA properties have been reviewed. Better crystallinity level can be achieved by the use of nucleating agents and plasticizers in association with suitable processing parameters. Mechanical properties could also been improved by the help of chain extension. Impact resistance to produce films and bottles will be enhanced according to additions of core shell rubbers. Temperature resistance and biodegradability can be carried with the use of clays to synthesize PLA composites. Blending PLA with other biomaterials are ways to be followed to produce tunable and economic biomaterials. Finally Chitosan is an interesting material to obtain, associated with PLA, good barrier properties for film applications.

## 2. Main results and discussions

The aim of the work was firstly to identify actual weaknesses of commercial grades of PLA. Secondly, pertinent ways to improve PLA's properties have been identified according to chosen process and final properties wished. The present study was composed of four main steps:

- *Academic bibliography of actual properties of PLA, its industrial synthesis and different ways of improvement of its physical, chemical and thermomechanical properties. According to this first step, PLA formulations to be synthesized and tested were determined. Raw materials and additives were also ordered.*
- *Four commercial grades of PLA from suppliers were characterized in order to compare their thermal, rheological, mechanical and physical properties. This study shows that commercial grades of PLA by their physical properties.*
- *Elaboration of PLA formulations was done at plastic manufacturing facilities of our laboratory using a corotating twin screw extruder. Blends were pelletized and then characterized using capillary rheometry , differential scanning calorimetry (DSC), thermomechanical analysis, ...*

- *Thin films were also prepared in order to characterize mechanical and thermomechanical properties of synthesized materials.*

*All formulations were done on the basis of Natureworks® LLC PLA grade 2002D (extrusion grade).*

The main objectives are:

- *Improvement of crystalline properties and crystallization kinetic was performed using nucleating agents (Talc) and plasticizer poly(ethylene glycol) PEG.*
- *Improvement of elongation at break and impact resistance of PLA was done using commercial Core-Shell rubbers grades (supplied by Rohm & Haas). Studied grades were Paraloid™ BPM500 (sold for PLA that keep its transparency) and Paraloid™ EXL2330 related in academic literature.*
- *Chain extension of PLA was performed using commercial additive supplied by BASF. This additive is patented by Naturworks® LLC and its name is Joncryn®. Joncryn® additives are multifunctional polymers containing epoxy functions). The effect of two grades of Joncryn® on PLA will be characterized: Joncryn® ADR 4300S (mid epoxy functionality) and Joncryn® ADR 4368CS (high epoxy functionality that certified FDA).*
- *Nanostructuring of PL by elaboration of nano or microcomposites using Montmorillonite nanoclays. The addition of chitosan (derived from chitin 2nd most abundant natural polymer worldwide) has also been explored as the 2nd composite way. Nanoclays, grade Nanofil® 5, was purchased from Southern Clay Products (Germany) and Chitosan of medium molecular weight was purchased from Aldrich.*

## 2.1. Material and Methods

### Classification, evaluation and selection of PLA grades available on the market.

The identification of PLA grades available on the market has been carried out specifying following aspects:

- *The place of production: US, Europe, Asia.*
- *Suitable processing technologies: extrusion, injection molding, thermoforming, etc.*

Following to this identification, four PLA grades have been chosen to be tested. These PLA grades fulfil following conditions:

- *From two different suppliers: one from US and the other one from Europe*
- *For each supplier, one grade for each of the two main processing technologies (extrusion, Injection molding and)*

### Classification, evaluation and selection of PLA grades available on the market.

Results of the identification of PLA grades available on the market are displayed below:

Supplier	Grades	Place of production	Suitable processing technologies
Natureworks	3001D	USA	injection molding
Natureworks	2002D	USA	extrusion, thermoforming
Natureworks	3051D	USA	injection molding
Natureworks	4032D	USA	extrusion, extrusion film
Natureworks	4042D	USA	extrusion, extrusion film
Natureworks	4060D	USA	co extrusion
Natureworks	7000D	USA	blow molding
Natureworks	7032D	USA	blow molding



Mitsui Toatsu Chemicals	LACEA H100 J unstretched	Japan	film, blow, injection molding
Mitsui Toatsu Chemicals	LACEA H100 J stretched	Japan	film, blow, injection molding
Mitsui Toatsu Chemicals	S100	Japan	
Mitsui Toatsu Chemicals	T100	Japan	
Jongboom	Biopearles M106		injection molding
Jamplast	Jamplast JPPLA		extrusion, thermoforming
Hycail	HM 1011	EU	extrusion, thermoforming, film extrusion and injection molding
Hycail	XP13003, XP13004, XP13005, XP12001	EU	blow molding, injection molding and paper coating
Metabolix	P1001	USA	
Metabolix	P1002	USA	injection molding
Metabolix	P2001	USA	extrusion coating

Table 1: Identification of PLA grades available on the market

Following the previous identification, 4 grades of PLA were selected (see table 4) to be tested and characterized.

	Injection molding	Extrusion
Natureplast	PLI005	PLE005
Cargill Dow, Natureworks®	3051D	2002D

Table 2: Selected PLA grades for characterization

Then, these four commercial grades were characterized in order to evaluate and classify them. Physico-chemical, thermal, mechanical and rheological properties have been investigated using the following analytical/testing methods:

- **Size Exclusion Chromatography (SEC)** to provide information in terms of molecular weight and polydispersity of selected PLA grades.
- **Differential Scanning Calorimetry (DSC)** with the aim to determine the thermal behaviour of selected PLA grades.
- **Melt Rheometry** to investigate viscoelastic properties of different studied PLA(s) (viscosity, relaxation, elasticity...)
- **Tensile test on PLA film** to determine some mechanical properties.
- **Dynamic thermomechanical analysis (DMA)** to emphasize impact of thermomechanical past on material properties.

### Classification, evaluation and selection of additives available on the market to improve PLA performance.

A preliminary work aiming at identifying weaknesses of commercial grades of PLA was necessary before the identification of additives available on the market to improve PLA performances. This work was composed of:

- *An identification of weaknesses of neat PLA that was carried out by a bibliography - current properties of PLA and its industrial synthesis – and completed by the characterization and the comparative study of four commercial grades mentioned in the previous part.*
- *An identification of different ways of improvement of its physical, chemical and thermomechanical properties thanks to an academic literature review.*

Following these identifications, 4 axes of improvement have been selected as essential to be studied:

- *Cristallinity and kinetic of cristallization*
- *Mechanical properties*
- *Thermomechanical properties*
- *Barrier properties*

Consequently, the identification of additives available on the market was oriented and based on the improvement of these axes:

- 1 Plasticizers and nucleants to improve **cristallinity and kinetic of cristalization**:
  - Plasticizers: P.E.G : poly(ethylene-glycol) from Alrich
  - Nucleants: Talc from Aldrich
  - EBHSA...(the results concerning this nucleant will not be presented in this paper (see our patent [1])
- 2 Chain extender to improve **elongation at break and impact resistance**:
  - Joncryl® J4368 CS and Joncryl® J4300 S from BASF
- 3 Core-Shell particles to improve **impact resistance and elongation at break**
  - Paraloid™ EXL2330 from Rohm&Haas
  - Paraloid™ EXL2314 from Rohm&Haas
  - Paraloid™ BPM500 from Rohm&Haas
- 4 Montmorillonite nanoclays to increase **elastic modulus** and, help **biodegradability**, flame retardant and **nucleating effect**
  - Nanofil® 5 from Southern Clay Products, GE
- 5 Chitosan to improve **barrier properties**
  - Medium Molecular Weight Chitosan powder from Aldrich

Formulations were defined varying proportions and blends were synthesized with the purpose of checking experimentally the efficiency of these additives to advance PLA properties.

All blends were made of the same PLA commercial grade, Natureworks® 2002D (extrusion grade), and were compounded in corotating twin-screw extruder at different compositions. Indeed, the blends were characterized in order to quantify the improvement of the rheological, thermo-mechanical and barrier properties. This experimental part has led to identify 3 additives and formulations showing interesting results.

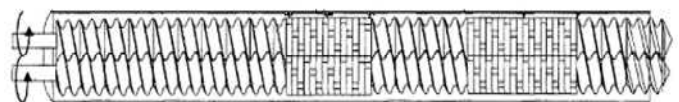


Figure 6: PRISM 16/25 corotating twin-screw extruder

Table 3: Summary of formulations and characterized blends

## 2.2. Results

### 2.2.1 Results of Size Exclusion Chromatography

These first results show that molecular weight distribution of Natureworks® grades is broader than these from Natureplast. Polydispersity index of Natureplast grades are very close and lower than 2. Figure 7 present a comparison between their molecular distributions. Table 3 summarizes the obtained molecular characteristics. Regarding the average molecular weight, values are quite similar except for Natureworks® injection grade (3051D) which show a large molecular distribution with a presence of small chains.

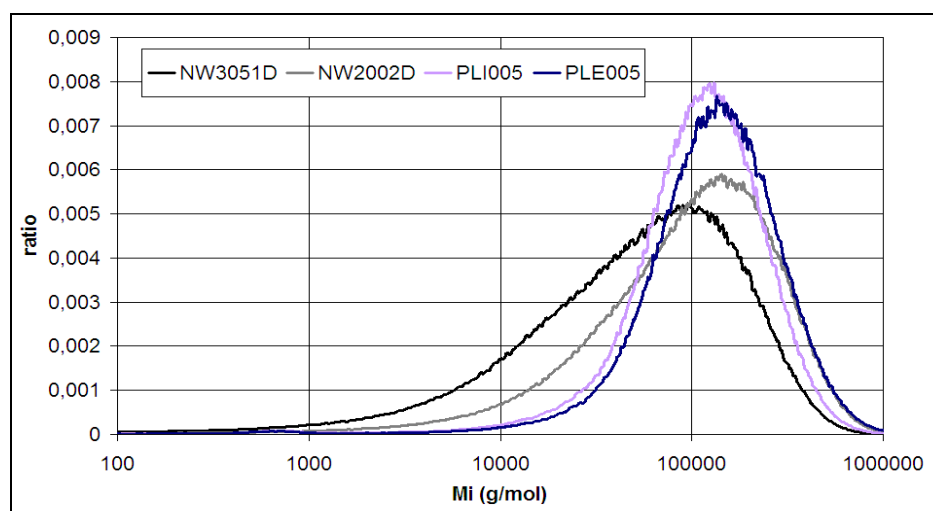


Figure 7: Overlap of  $M_i$  distribution curves

Matière	Mp	Mn	Mw	Ip
NW3051D	96580	25885	111300	4,3
NW2002D	144510	61255	167035	2,73
PLI005	131730	90190	155075	1,72
PLE005	137075	110380	183665	1,66

(Mp: molecular weight at peak; Mn: number average molecular weight;  
Mw: weight average molecular weight; Ip: polydispersity index)

Table 3: results of Mp, Mn, Mw and Ip

### 2.2.2. Results of Differential Scanning Calorimetry

The thermal analysis was performed in two parts:

- 1<sup>st</sup> part: pellets were analysed without any thermal treatment. They were just dried approximately 12 hours in an oven at 60°C under vacuum conditions and also to relax chains before to be analyzed.
- 2<sup>nd</sup> part: pellets were analysed again after having been submitted to one of the following thermal treatments:
  - Treatment 1: pellets were melted at 190°C and then annealed at 110°C overnight
  - Treatment 2: pellets were annealed at 110°C overnight

A melting peak is observed for all grades on first heating thermograms. However, this peak is much more important and noticeable for Natureworks® grades than Natureplast ones. The calculated crystalline phase is about 38% for Natureworks® grades and less than 5% for Natureplast grades (table 4). Therefore, PLAs from Natureworks® exhibit higher crystalline content than Natureplast products in «recieved» conditions. This observation cannot be generalized to purchase conditions since we do not have any information about exact storage conditions between purchase and the moment pellets were received to be analysed. Then, during cooling and second heating, any recrystallisation or melting phenomena are observed. The slow crystallisation kinetics of PLA (frequently related in literature) is emphasized with these tests. According to the present results, Natureplast products have a glass transition temperature slightly lower than Natureworks® products (about 2°C). Same phenomenon is observed for melt temperature: PLA from Natureworks® present a higher melt temperature (7°C to 10°C) than PLA from Natureplast.

Results	1st heating			2nd heating	
	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)	X <sub>c</sub>	T <sub>g</sub> (°C)	ΔC <sub>p</sub> (W/g)
NW3051D	153	34,9	0,38	61	0,092
NW2002D	152	34,9	0,38	61	0,093
PLI	142	4	0,04	59	0,088
PLE	144	1,6	0,02	59	0,083

T<sub>m</sub>: Melting temperature (°C); ΔH<sub>m</sub> : melting enthalpy (J/g) ;

X<sub>c</sub>: crystalline amount (using 93 J/g as reference value for a crystallite of infinite size);

T<sub>g</sub> (°C): glass transition temperature

Table 4: Comparison of thermal properties of selected PLA grades – 1st part (without any treatment)

#### **Regarding the 2<sup>nd</sup> part:**

The results given in table 5 show that samples which have been melted before annealed have a bigger crystalline content than samples only annealed. This could be explained by an enhancement of crystallisation when samples were cooled between 190°C and 110°C. Moreover, it seems that all analysed samples reach the same maximum crystalline content that is about 40%. Consequently, it is possible that Natureworks® sells pellets that have been thermally treated before since previous analysis results show a similar level of crystallinity. Such treatment is probably necessary to obtain semicrystalline products and so, helpful for material processing to improve mechanical and barrier properties. Additionally, results of this second part confirm observations done in the first one:

- a glass transition temperature slightly lower for Natureplast materials (about 2°C)

- a melt temperature lower for Natureplast products than Natureworks® (about 7°C to 10°C)

	Material	1st heating			2nd heating
		T <sub>m</sub>	ΔH <sub>m</sub>	X <sub>c</sub>	T <sub>g</sub>
treatment 1	NW 3051	153,2	38,1	0,41	60,8
	NW 2002	152,2	36,3	0,39	61
	PLI005	146,3	38,5	0,41	58,1
	PLE005	147,8	40,3	0,43	58,3
treatment 2	NW 3051	154,4	34,3	0,37	61,6
	NW 2002	154,1	31,9	0,34	61,3
	PLI005	144,7	32,2	0,35	59,4
	PLE005	147,8	36,5	0,39	59,2

T<sub>m</sub>: Melting temperature (°C); ΔH<sub>m</sub> : melting enthalpy (J/g) ;

X<sub>c</sub>: crystalline amount (using 93 J/g as reference value for a crystallite of infinite size);

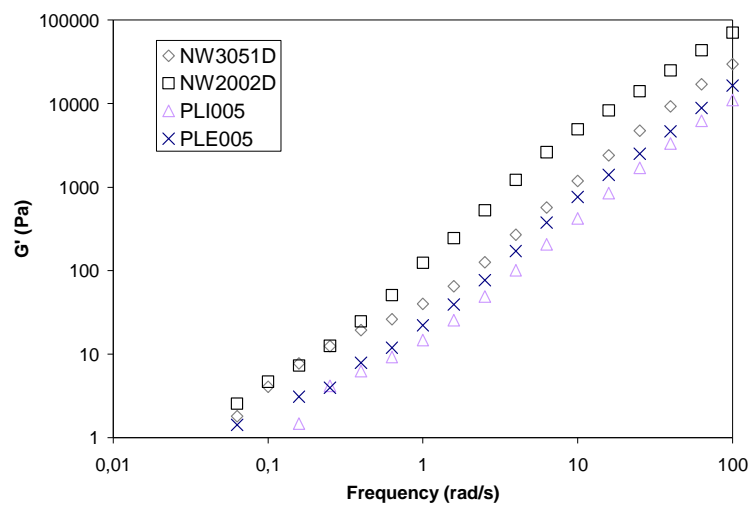
T<sub>g</sub> (°C): glass transition temperature

Table 5: Comparison of thermal properties of selected PLA grades – 2nd part (after treatment)

### 2.2.3. Results of Melt Rheometry

Storage modulus ( $G'$ ), loss modulus ( $G''$ ) and complex viscosity ( $\eta^*$ ) as frequency function are presented as follow. These results show that Natureplast and Natureworks® materials have not the same rheological behaviour. One common phenomenon observed on curves for each supplier is that  $G'$  and  $G''$  of extrusion grades are slightly higher than injection grade. Moreover  $G'$  and  $G''$  of the two Natureworks® grades are bigger than  $G'$  and  $G''$  of Natureplast grade. Complex viscosity curves showed again the contrast of Natureplast and Natureworks® properties. These results corroborate those obtained from SEC investigations.

Storage modulus -  $G'(\omega)$ :



Complex viscosity -  $\eta^*(\omega)$ :

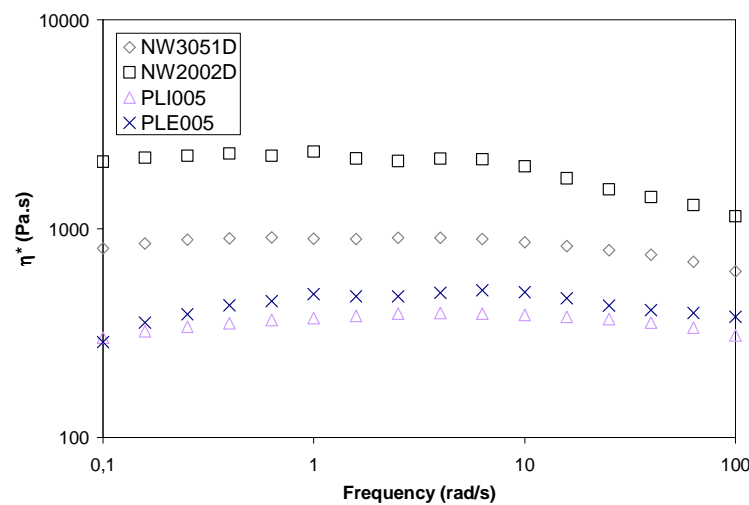


Figure 8: Comparison of the rheological behavior of the 4 industrial grades at 180°C.

### 2.2.5. Results of the dynamic thermomechanical analysis

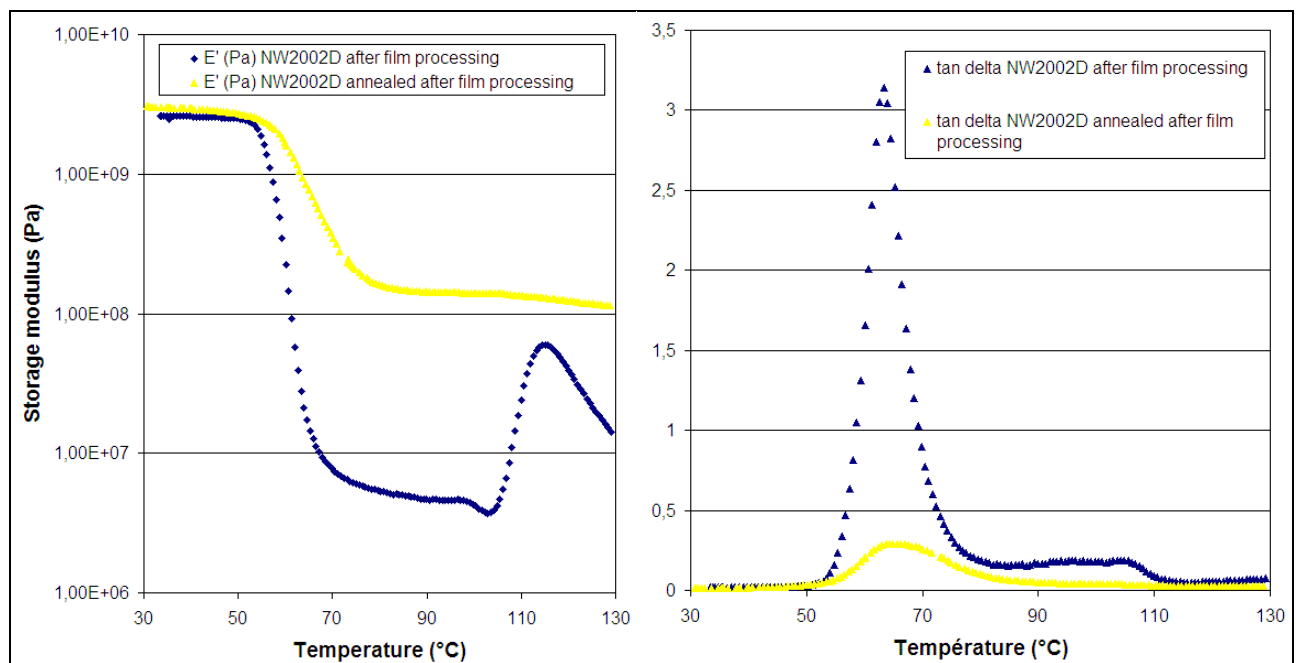


Figure 9: DMA results (Storage modulus  $G'$  and  $\tan\delta$ ) on PLA film with and without annealing

The results given in Figure 9 emphasize the influence and impact that process could have on material properties. Thermomechanical properties depend on thermomechanical past, so process conditions. PLA properties depend on its thermomechanical past as well; we can see that the PLA film analyzed was converted under process conditions that did not allow the material to crystallize (thermally or mechanically under stress) leading to the detection of high  $\tan\delta$  peak (glass transition/amorphous state). Nevertheless, annealing step performed is efficient enough to allow the PLA film to crystallize since  $\tan\delta$  has dramatically decreased.

To conclude, this first study showed that Natureplast injection and extrusion grades are not equivalent to Natureworks® extrusion and injection grades. Materials showed differences in each experiment carried out. Chromatography showed that Natureworks® products have high polydispersity especially extrusion grade 2002D. DSC thermograms showed that “as received” materials are semi-crystalline for Natureworks® pellets and amorphous for Natureplast pellets. Mechanical tensile tests showed slight differences in terms of properties. The rheological analysis confirms these differences between materials. Finally, thermomechanical properties (especially the modulus) are increased. It's due to the presence of crystalline phase induced by annealing.

### 2.3. Classification, evaluation and selection of additives available on the market to improve PLA performance.

#### 2.3.1. Identification of PLA weaknesses and ways of improvements

The academic literature review about PLA's properties and weaknesses as well as the different ways for improvements can be seen in **the state of the art**; the main observations are summarized below:

*Concerning PLA properties and weaknesses:*

Based on commercial grade characterized and studied in the previous part, PLA can be amorphous or semi-crystalline. When PLA is semi-crystalline, maximum amount of crystalline phase is about 40%. Its glass transition temperature is about 60°C and melting point is approximately 150°C. These poor thermal properties represent one of the main weaknesses of PLA (regards to PET for example that has a glass transition temperature at 80°C approx and crystalline melt at 250°C approx.). This weakness does not allow PLA to be used to make microwavable packages. One other weakness of PLA it is very slow crystallization kinetic that didn't allow it to crystallize during its transformation by extrusion, injection or thermoforming. Some mechanical properties of PLA are also poor. PLA has satisfactory elastic modulus and stress at yield. But it has a very small elongation at break (some percent) and a very poor resistance to impact regards to classic polymers used for packaging. That put another brake on using PLA for some applications. Last of the main weakness of PLA are its poor barrier properties to oxygen, gazes and water vapor regards to PET for example.

*Concerning ways to improve PLA properties:*

Ways to improve PLA properties according to academic literature are:

- Improvement of **crystalline properties and crystallization kinetic** of PLA is performed with the help of **nucleating agents** (crystallization initiator) and **plasticizers** (to enhance macromolecular mobility).
- Improvement of **elongation at break** and **impact resistance** is performed by the addition of **core shell rubbers particles**.
- **Chain extension of macromolecular chain** of PLA may help **strength of melt** and **thermomechanical properties** of PLA by decreasing molecular mobility. This chain extension can also be performed using **molecules containing epoxy or isocyanate functions**.
- **Composites materials** based on PLA may have better **thermomechanical behavior, barrier properties** and **kinetic of biodegradability**.

### 2.3.2. Experimentation and characterization

It is important to note that the following results are not exhaustive. Despite the interesting nature of this kind of main results, only some ones are chosen to be presented here as follow:

#### A- Blends with plasticizers

Blends of PLA + 10% wt PEG and PLA + 1% wt Talc have been prepared. Their main thermal, and mechanical characterizations are given in figures (10-13) and table 06, respectively. Hence, the following comments can be noted:

→ *Crystallization kinetic of PLA was improved according to the use of nucleants and plasticizer.*

→ *Crystallization half time of PLA with TALC or PEG are shorter than neat PLA*

→ *Using PLA with TALC :*

- Better crystallization half time (but a little bit long for processing)
- Mechanical behavior is weaker than neat PLA
- Spherulite size is about 50 µm within a long annealing time and appropriate temperature

→ *Using PLA with PEG :*

- Crystallization half time is too long
- Tg is too much lowered with 10% wt. of plasticizer
- Spherulite size is about 200µm within a long annealing time and appropriate temperature

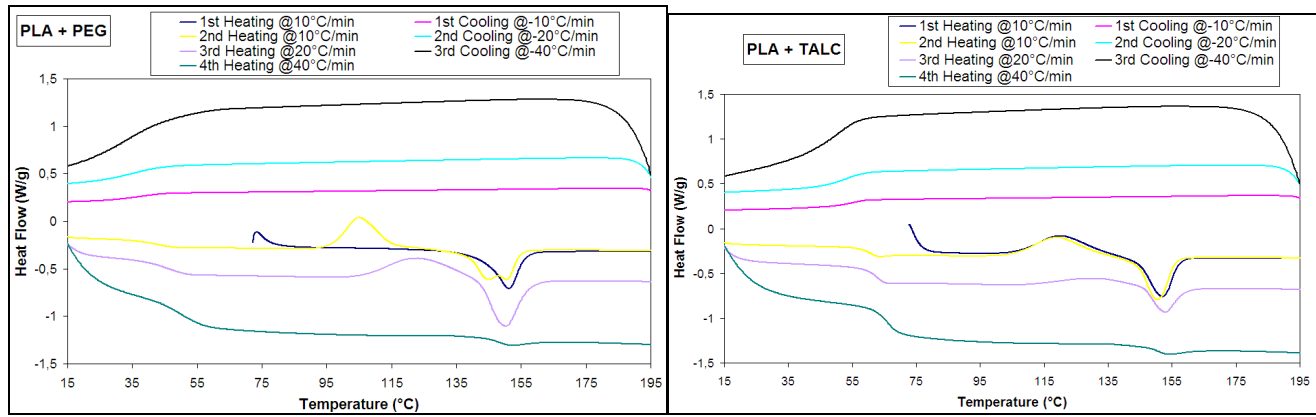


Figure 10: Result of DSC analysis –influence of the heating rate

	E (Mpa)	$\sigma_y$ (Mpa)	$\epsilon_y$ (%)	$\sigma_r$ (Mpa)	$\epsilon_r$ (%)
NW2002D	2540 (210)	54,6 (2,1)	3,1 (0,1)	47,3 (1,8)	27 (15)
PLA + 10% wt. PEG	1880 (16)	44,6 (0,8)	3,6 (0,1)	25,3 (2,9)	162 (130)
PLA + 1% wt. TALC	2480 (110)	48,4 (2,0)	3,2 (0,1)	42,9 (1,3)	12 (3)

Table 6: Tensile test results – comparison of mechanical properties

Finally, it is important to note that the original ternary nucleant systems based on talc, EBHSA and PEG to enhance the kinetic of crystallization of PLA in correlation with processing technology [Maazouz et al. [1]].

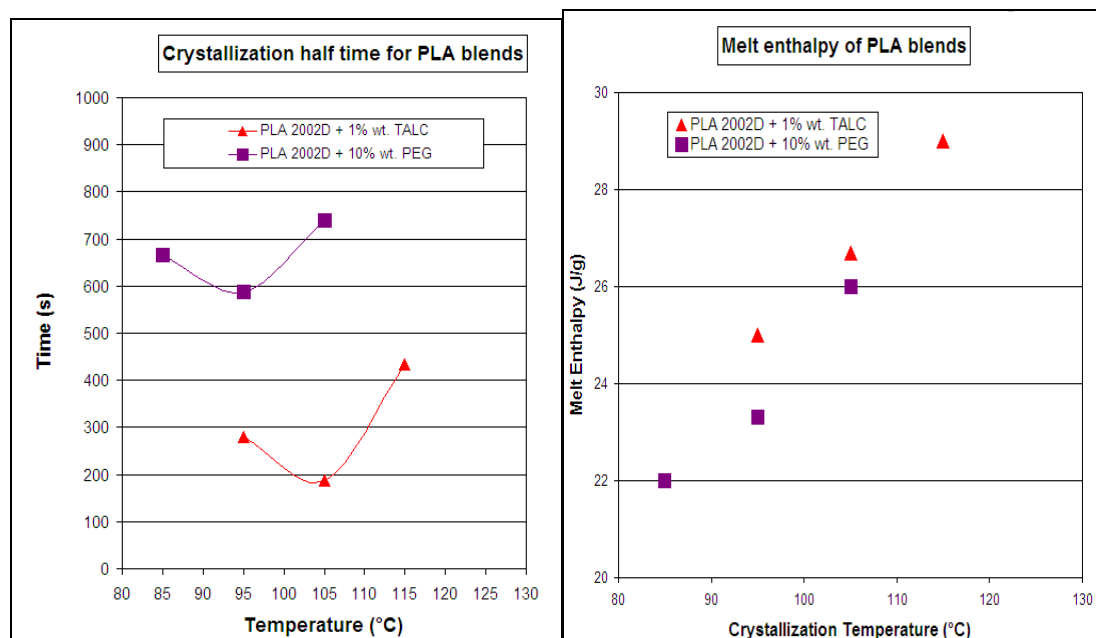


Figure 11: determination of crystallization half time



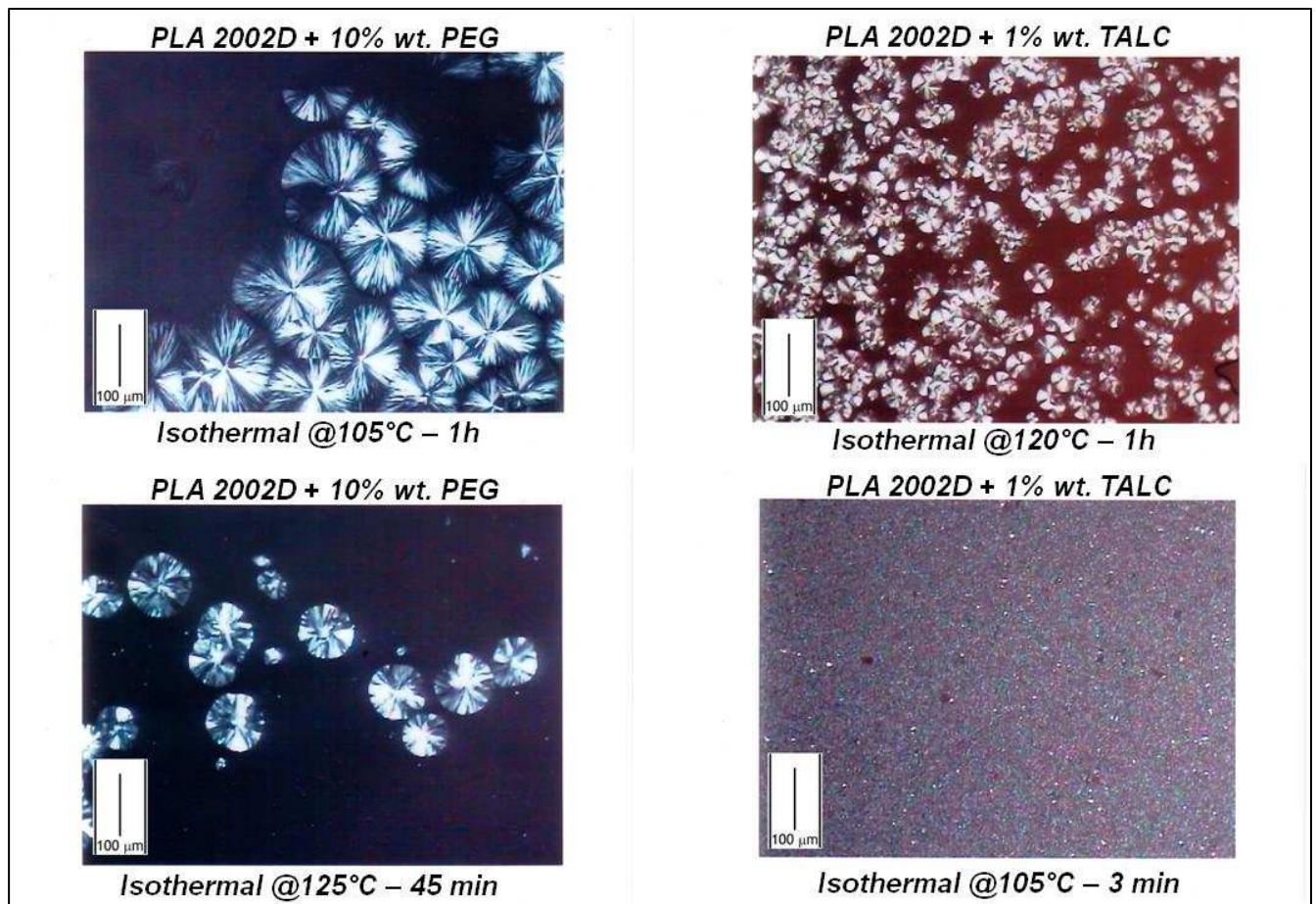


Figure 12: Polarized Light Microscopy observation (Before isothermal crystallization every samples were melted @200°C during 5 min)

**B- Blends with chain extenders:**

Blends of PLA with 0.9% wt. Joncryl J4368 CS (FDA), PLA with 0.5% wt. Joncryl J4368 CS (FDA), PLA with 0,9% wt. Joncryl J4300 have been also formulated. Their main thermal, rheological and mechanical characterizations are given in figures (13-15) and table 7. Hence, the following comments can be noted:

- + *Mechanical properties improved ( $\sigma_y$  and elasticity modulus)*
- *Extrusion process may be difficult to control*
- *0,9% of Joncryl ® J4368 CS in Natureworks 2002D is too high*
- - *No nucleation role*

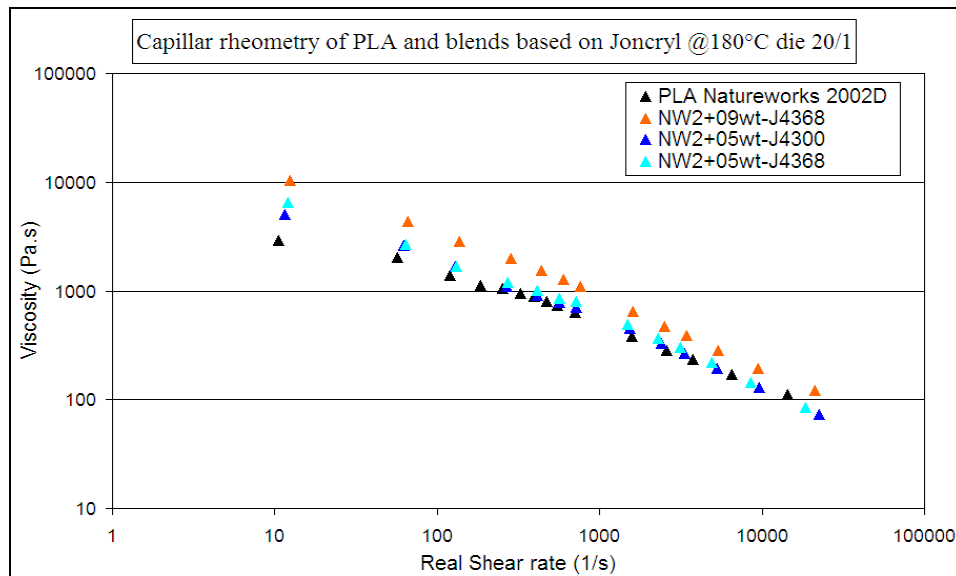


Figure 13: Results of capillar rheometry analysis of the neat PLA and its formulation with the chain extender.

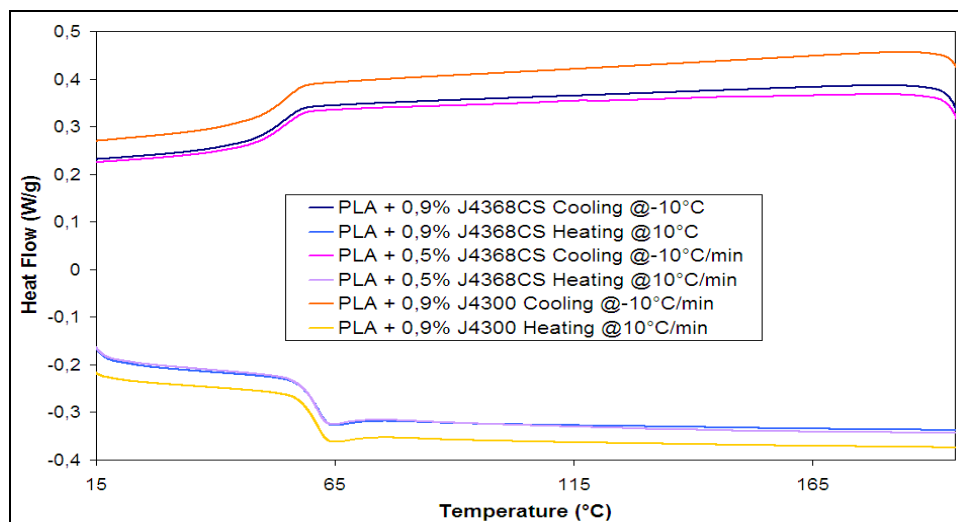


Figure 14: Result of DSC analysis of the formulations based on PLA and the chain extender at different compositions.

	E (Mpa)	$\sigma_y$ (Mpa)	$\epsilon_y$ (%)	$\sigma_r$ (Mpa)	$\epsilon_r$ (%)
NW2002D	2540 (210)	54,6 (2,1)	3,1 (0,1)	47,3 (1,8)	27 (15)
PLA + 0,9% J4368CS	2510 (150)	63,1 (1,8)	4,0 (0,1)	43,6 (7,4)	9 (5)
PLA + 0,5% J4368CS	2880 (110)	61,5 (1,1)	2,9 (0,1)	48,4 (5,2)	18 (5)
PLA + 0,9% J4300	2810 (170)	58,2 (3,3)	2,9 (0,1)	50,2 (2,6)	29 (10)

Table 7: Tensile test results – comparison of mechanical properties

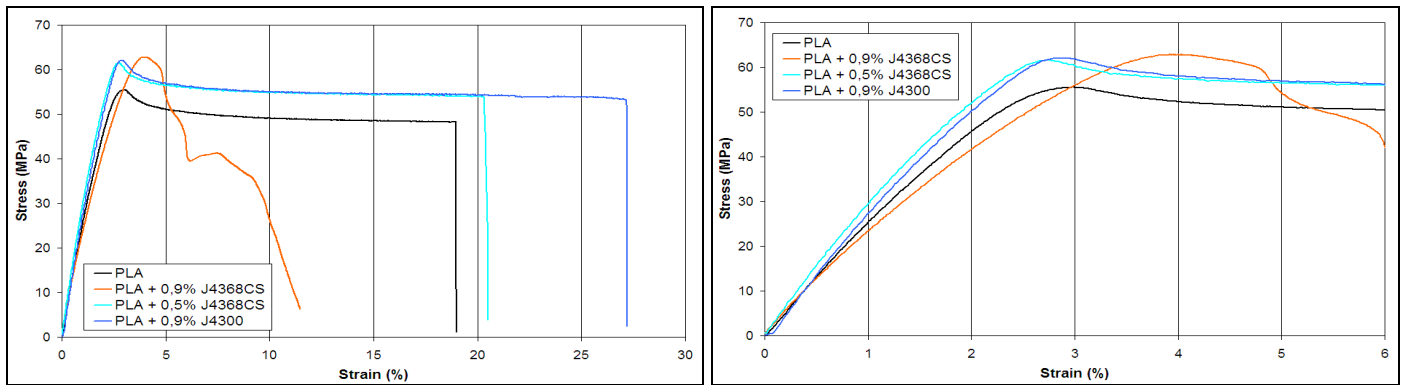


Figure 15: Tensile test curves of the formulations based on PLA and the chain extender at different compositions.

### C- Blends with Core Shell particles:

The following formulations have been prepared:

- PLA with 10% wt. Rohm&Haas BPM500
- PLA with 5% wt. Rohm&Haas BPM500
- PLA with 10% wt. Rohm&Haas EXL2330
- PLA with 5% wt. Rohm&Haas BPM500 + 0,5% wt. J4368CS

Their main thermal and mechanical characterizations are given in figures (16-17) and table 8. Based on these results, the following comments can be noticed:

++ Better processability

++ Better elongation at break without lowering  $T_g$

+ Good visual transparency with Paraloid<sup>TM</sup> BPM500

- Decrease of elastic modulus and  $s_r$

-- No nucleation role

	E (Mpa)	$\sigma_y$ (Mpa)	$\epsilon_y$ (%)	$\sigma_r$ (Mpa)	$\epsilon_r$ (%)
NW2002D	2540 (210)	54,6 (2.1)	3,1 (0.1)	47,3 (1.8)	27 (15)
PLA + 5% BPM500	2130 (100)	49,7 (1.2)	3,3 (0.2)	34,8 (0.6)	49 (7)
PLA + 10% BPM500	2030 (70)	54,6 (0.4)	4,0 (0.1)	38,0 (2.2)	174 (110)
PLA + 10% EXL2330	1950 (NM)	48,4 (NM)	3,5 (NM)	37,0 (NM)	178 (NM)
PLA + 5% BPM500 +0,5% J4368CS	2250 (50)	50,1 (0.8)	3,0 (0.2)	40,7 (1,2)	29 (6)

Table 8: Tensile test results – comparison of mechanical properties

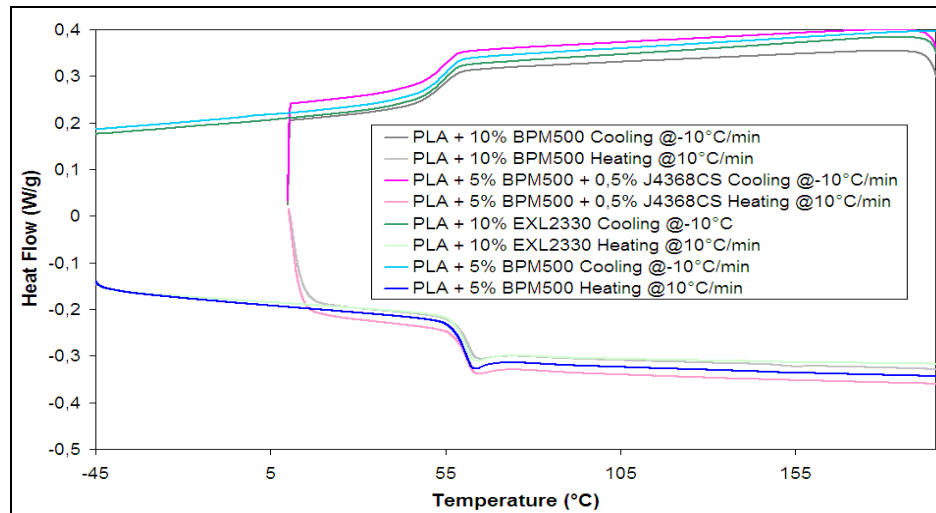


Figure16: Result of DSC analysis of PLA and its formulations with 5 and 10% o a core shell

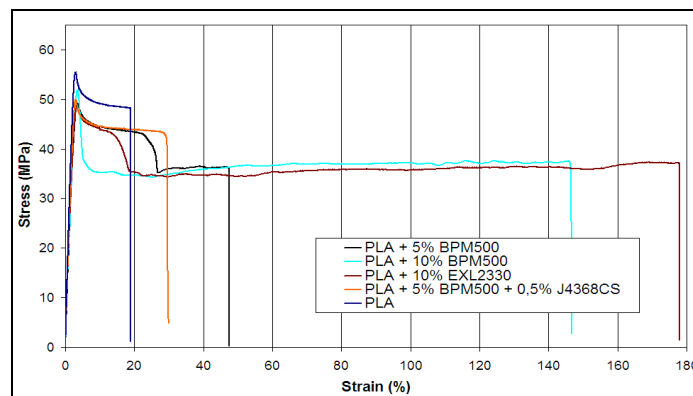


Figure 17: Tensile test curves

### D- Blends with Nanoclays / Chitosan:

Blends of PLA with 5% wt. MMW Chitosan and PLA with 5% wt. Montmorillonite Nanofil® 5 have been also formulated by twin screw extruder too. Their main thermal and mechanical properties are presented in figure 18 and summarized in table 9, respectively. Indeed, the following comments can be noted:

+ *Small nucleating role of Chitosan and Montmorillonite*

+ *No problems during processing*

- - *lower mechanical properties except elastic modulus for PLA + MMT*

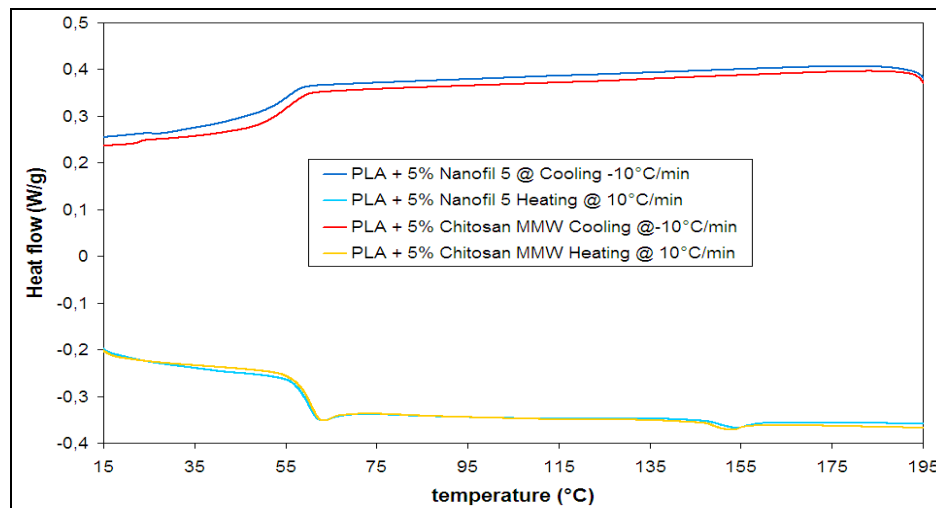


Figure 18: Result of DSC analysis of PLA\_Blended Nanoclays and Chitosan.

	E (Mpa)	$\sigma_y$ (Mpa)	$\varepsilon_y$ (%)	$\sigma_r$ (Mpa)	$\varepsilon_r$ (%)
NW2002D	2540 (210)	54,6 (2,1)	3,1 (0,1)	47,3 (1,8)	27 (15)
PLA + 5% CTN	1830 (20)	41,9 (0,6)	3,2 (0,1)	38,2 (0,8)	7 (1)
PLA + 5% Nanofil 5	2620 (100)	46,9 (2,0)	2,6 (0,1)	39,6 (1,4)	15 (4)

Table 12: Tensile test results – comparison of mechanical properties

## 4. Conclusion

The study of four commercial grades of PLA, related previously, showed that PLA grades may have some differences in their properties (thermal, rheological, mechanical and physical). So these differences have to be taken into account in order to choose the right grade of PLA according to process and final application chosen.

The study of PLA with additives in order to enhance thermomechanical properties of PLA gave these results:

- 1) Plasticizer (PEG) helps to processability of PLA lowering torque of extruder. Elongation at break is significantly improved. Crystallization kinetic is also improved, but not enough (study on nucleating agents may enhanced this kinetic). Nevertheless the addition of plasticizer brought to weaknesses. The glass transition temperature is lowered from 60°C (neat PLA) to 44°C within the addition of 10% wt. of PEG. Elasticity modulus is also too much lowered. As a conclusion for this part, the use of plasticizer only with PLA except if no thermal properties are required.
- 2) Nucleating agent (TALC) helps PLA's nucleation initiation but the addition of TALC lowers the elongation at break of PLA. We were able to use the ternary nucleating system, based on talc, EBHSA and PEG to enhance the kinetic of crystallization of PLA in correlation with processing technology [1].

- 3) *The addition of Core-Shell grade BPM500 lowered melted viscosity. In the case of grade EXL2330, no difference were measured compared to neat PLA. Core-Shell didn't act as a nucleating agent. Elongation at break is improved as when a plasticizer is used but without lowering Tg. Elastic modulus of this blend is lower than neat PLA but as not as when a plasticizer is used (for same amount of additive). Visual observation of film confirms that grade BPM500 keeps PLA's transparency better than EXL2330. Study of impact resistance has to be done.*
- 4) *Chain extension of PLA with BASF Joncryl® additives improves elasticity modulus and stress at yield. High reactivity of blend at the molten state at low shear rate may affect its transformation when processing by extrusion. Added at low rates (< 0.5% wt.) it can "repair" molecular degradation (well known when processing polyesters). It could also be used as a compatibilizer when blending PLA with other molecules. No role of chain extender as nucleation initiator was measured.*
- 5) *The last two blends studied (PLA + Nanoclays or PLA + Chitosan) brought a small nucleating effect. Measured mechanical properties are lowered regards to neat PLA (not in the case PLA + nanoclays for which elasticity modulus is slightly improved). Nevertheless interesting enhancements that can be brought to PLA (bactericide and fungicidal for chitosan and help to biodegradation and enhancement of thermo-mechanical behavior) need a much more precise study over these blends.*

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