Crystallization of Poly (Lactic Acid), PLA: Effect of Nucleating Agents and Structure-Properties Relationships

Marwa Abid, Benoit Mallet, Khalid Lamnawar* and Abderrahim Maazouz*

Ingénierie des Matériaux Polymères IMP, UMR 5223, INSA Lyon, University of Lyon, Villeurbanne, France.

Abstract: In this paper, a brief state of the art is given firstly on structure-processing-properties relationships on PLA. Secondly, a specific focus is devoted on some recent and not yet unpublished recent work regarding the isothermal and non-isothermal crystallization behaviors of the poly (lactic acid). Thereby, they were investigated by differential scanning calorimetry. The effect of heterogeneous nucleation was assessed by additive talc, ethylenebis (12- hydroxy stearyl amide) (EBHSA) and polyethylene glycol (PEG) as potential nucleating agents. Thus, the improvement of crystallization kinetics under isothermal crystallization was described by the Avrami equation. A new formulation system can be used as a nucleating agent. This system consists of (1% wt talc, 1% wt PEG and x% wt EBHSA), “x” is equal to 1, 3 and 5%. Startling, Its increase the crystallization rate of pure PLA and reduce drastically its half-time of crystallization. Hence, the obtained results are for the great interest of some biopolymer processing as well injection molding or extrusion.

Keywords: Poly (lactic acid), Crystallization kinetics, Nucleating agents.

INTRODUCTION

Poly (lactic acid) (PLA) is a promising polymer as a bio based and biodegradable material. It has received much attention in the research of biodegradable polymers. The expected rise in the cost of petroleum opens a bright perspective for this material. Indeed, PLA have a good clarity and glossy, moderate taste and flavor barrier and high strength enough stiffness to produce hard package because it is synthesized from annually renewable resources.

Products with short life-times, such as food packaging, should obviously last no longer than a few months, and compostable polymers such as PLA can allow this kind of life cycle regulation, thereby helping to reduce the huge amount of nonrecycled plastic material.

Although PLA is already commercially available, this biobased polyester needs to see some of its properties improved in order to be used in a wider application field. Its brittleness and its weak melt properties limit its use to products obtained by smooth melt processing techniques such as injection molding or film extrusion. Melt stretching processes typically bi-oriented film extrusion or film blowing would on the other hand require higher melt strength. One of the most investigated ways of coming to terms with this draw-back is the chain extension/branching of PLA [1-6].

This study has therefore been dedicated to the investigation of the thermal properties of some molecularly modified PLAs. The thermal properties of those modified materials were expected to differ from the neat PLA since the molecular weight and the branching structure of a semi- crystalline polymer are known to influence its thermal behavior [7-14]. Several investigations based on branched/extended materials have highlighted the positive influence of this kind of chain modification on the crystallization kinetics of polymers. Nam *et al*. [13] and Dorgan *et al*. [7] reported that, respectively for PP and PLA, the corresponding branched materials have an increased overall crystallization kinetic as compared to their linear counterparts. McKee *et al*. [11] explained this phenomenon by a nucleation enhancement Heterogeneities created by the branching process were believed to be one of the reasons behind the changes in the thermal behavior of the polymer.

Similarly, Krumme *et al*. [9] reported that a modification of the dispersity D such as a bimodal population was seen to increase the nucleation density for PE. Hang Gi *et al*.[8], Chen *et al*. and Miyata *et al*. [12] worked on polyesters, respectively Poly (butadiene adipate) (PBA), Poly (trimethylene teraphtalate) (PTT) and Poly (L-lactic acid) PLLA, and found a drastic improvement of the spherulitic nucleation density coupled with a reduction of the spherulitic growth rate when the molecular weight was increased. Investigation of the thermal transitions and the crystallization process by bulk calorimetry, optical and thermo mechanical analysis, as carried out in the present study, should thus provide clear information regarding the thermal behavior of neat and chain-extended PLAs.

---

*Address correspondence to this author at the Ingénierie des Matériaux Polymères IMP, UMR 5223, INSA Lyon, University of Lyon, Villeurbanne, France;
E-mail: Khalid.lamnawar@insa-lyon.fr; abderrahim.maazouz@insa-lyon.fr

E-ISSN: 2312-5470/18

Moreover, Al Itry *et al*. [16] showed the effect of the film blowing process on the crystalline and thermomechanical properties of PLA/PBAT blends. Walha *et al*. [17] worked on PLA and found a drastic improvement of the melt strengthening without any chemical modification, and demonstrated that the blow film extrusion process improved the crystalline ability of PLA. Also, Lamnawar *et al*. [18] proved that the incorporation of Joncryl led to an enhancement of the blowing processing windows of PLA and this enhancement is probably due to the chain extension/branching phenomenon.

On the other hand, PLA showed major weakness which have to be improved in order to use it in many applications:

- Poor melt properties: Thermo/mechanical plasticization is the first step of any polymer melt processing. For PLA, this is a critical stage since the polymer is sensitive to thermal degradation [19, 20]. As a result, the processing temperature window is quite narrow; basically between 160 and 200°C. Following this melting phase, specific processing techniques such as foaming, blow molding or film blowing, require a sufficient melt strength for an efficient shaping. Unfortunately, PLA features a limited melt strength, and shape defects, including bubble instability in film blowing or cell collapse in extrusion foaming, are often encountered.
- Poor ductility: As reported in the section on mechanical properties, PLA is a brittle material with a low elongation at break (< 10%) and a high tensile modulus (> 3.5 GPa). As numerous applications require flexibility (*e.g*., packaging films, bags…), PLA would need to be blended with plasticizers or other biopolymers with lower glass transition temperatures (Tg). Disregarding the increase in the final product price, this combination can result in an alteration of the biodegradation rate, an instability of the mechanical properties with aging and a decrease in the strength and modulus of the plasticized PLA.
- Poor thermal resistance: The thermo-mechanical softening point for PLA lies around its glass transition temperature (*i.e*., ~60°C). This non-limiting parameter for biomedical applications becomes a real drawback for its use in hot environments, such as for food packaging or electronic housings. A substantial improvement can be obtained by employing nucleating agents and optimizing the crystallization process as described in a patent from Natureworks dealing with the enhancement of the crystalline ratio of thermoformed PLA sheets [21]. Such an improvement would be compulsory for hot-filled food trays or cups for hot liquid, for instance. Reinforcement with natural fibers has also been studied in order to compensate for the thermal weakness of the matrix [22, 23].
- Poor gases barrier properties and its low crystallization rate which restrict its development and practical applications.

This polymer has many challenges; one of the major issues limiting the wide-spread use of PLA is its cost. Because of an expensive monomer (lactic acid) production and the fact that the polymerization process is still in its early years, this bio polyester is not yet cost effective as compared to oil-based polymers. While the producers of biomedical PLA grades (*e.g*., Boeringer (DE), Purac (NL)…) are able to balance this costly process with the high value of the final products, the development of a large-scale production, in order for PLA to be utilized as a commodity plastic, is still in progress. Apart from the technical issues related to a cheaper production, various institutional regulations could lead to bioplastics being highlighted. The establishment of new waste management policies could promote their use for short-life and unrecycled packages. Even plastic transformers and/or customers can improve this status by using such polymers for short-life products (*e.g*., meat packaging, catering cutlery, waste bags…). Nowadays, bioplastics only have an ecological image with regard to marketing, without any integration in waste management (*i.e*., no acceptance in the composting plant, no recycling network). In addition, strong competitors to bioplastics are the postconsumer- recycled polymers. An improved plastic waste regulation would identify specific applications for these two types of eco-friendly polymers.

An enhancement of PLA properties remains a challenging domain for both academic and industrial research. The main concerns involve the crystallization, the mechanical and the gas barrier properties of PLA. Regarding the mechanical properties, the major challenge would be to achieve a durable toughening without compromising the tensile strength, modulus or biodegradability. PLA crystallization is also well-documented and a tuning of the thermal properties is possible by varying the stereo-regularity or using nucleating/plasticizing agents. Nevertheless, the crystallization rate and ratio still remain too low for a competitive production of heat-resistant products on industrial lines. The use of stereo complexes for crystallization is promising [24, 25] but is not yet industrially viable. Finally, the gas barrier properties could bring a valuation of PLA, especially in the food packaging domain. As an increased crystallization does not raise this last property enough, some new strategies have been put forward, *e.g*., a metal-oxide (SiOx,, Al2O3) surface treatment by atomic layer deposition, electron beam evaporation, magnetron sputtering or sol–gel coating [26, 27]. On the other hand, the use of nanoparticles has also been reported by Sinha Ray *et al*. as an efficient gas barrier enhancer for PBS [28] and is believed to have the same effect on PLA.

Therefore, considerable efforts have been made to improve the properties of PLA so as to compete with low-cost and flexible commodity polymers. One of these attempts was carried out by means of improving the crystallinity of PLA by adding nucleating agents. It is well known that the crystallization of crystalline polymers is one of the important characteristics because it affects the processability and the productivity of mold processing. Thus, this increasing is essential for the production of low-cost PLA-based materials with high thermal stability. Varying types of nucleating agents such as talc, EBHSA and PEG were used to improve the crystallinity of PLA: Talc is widely used nucleating agent. It was shown that talc nucleates the crystallization of polymers through an epitaxial mechanism. In the case of PLA, it is shown that it is possible to reach the 40% of crystalline phase and to reduce significantly the crystallization half-time when 1% talc is added.

Recently, another nucleating agent can nucleate the crystallization of PLA referring to recent researches which is ethylenebis (12- hydroxy stearyl amide). This compound has a melting temperature similar to that of PLA but is able to crystallize faster upon cooling.

Poly (ethylene glycol) PEG is the most studied like plasticizer and nucleating agent. It shows the best results at 10%wt. The presence of a plasticizer decreases the glass temperature and improves its ductility and drawability thus broadening the range of potential applications. In our case, PEG was used in the blend at different percentages (1%wt, 3%wt and 5%wt). For this reason, the efficiency of plasticization is not too remarkable. Lamnawar *et al*. [29-32] proposed a formulation of different nucleating agents that improved the crystallization kinetics. This formulation was composed of 1 wt% of EBSA, 1 wt% of TALC, and 10 wt% of PEG, which were blended to PLA.

Another way to improve properties of PLA reported in literature is chain extension, it increases molecular weights of polymer and strength of melt. This chain extension can also be performed using molecules containing epoxy or isocyanate functions. Moreover, Nano structuration can be considered as a way to improve that behavior of PLA by adding core shell rubbers particles and the last way is PLA blending with composite materials in order to increase the thermomechanical behavior, barrier properties and kinetics of biodegradability [29-32].

In this paper, we investigated the effect of nucleation on the crystalline content developed in isothermal and non-isothermal conditions. The crystalline content and properties achieved in different conditions are compared using a specifically formulations. Herein, the originally of the present approach is dealing with a correlation structure-processing- properties relationships. Some promising results will be drawn to overcome the PLA drawbacks.

MATERIALS AND METHODS

Materials

A commercial grades of poly (lactic acid) PLA supplied by Nature Works was a semi- crystalline grade (For the clarity purpose of the present paper, only results with a PLA 3051D will be presented). It exhibits a density of 1.25g/cm^3, a glass transition temperature and melting point of 57 and 153°C (differential scanning calorimetry DSC) respectively. Talc, EBHSA and PEG were evaluated as potential nucleating agents.

Blend Preparation

The neat PLA was pre-dried in vacuum oven at 80°C for 4h before use. Melt blending was performed at 200°C in a co-rotating twin-screw extruder at 100 rpm rotation speed. Prior to blending, the PLA was dried at 80°C for 4h in a desiccant dryer while the nucleating agents were used as received. PLA and nucleating agents were mixed together with different ratios of 99/1, 95/5 which is mean 1% wt and 5%wt of nucleating agents. Other blends were prepared by using a mixture of these three additives while fixing at 1% wt the percentage of talc and PEG in the blend and varying that of EBHSA (2%wt, 3%wt and 5%wt). The residence time of the blend in the extruder did not exceed 3 minutes in order to minimize the degradation during processing. Then, the mixtures were injected into specimens. The samples were dried at 60°C for 12h prior to DSC analysis.

Thermal Analysis

The thermal characteristics of the neat and plasticized PLA were determined using a differential scanning calorimeter (DSC Q100, TA instruments) in nitrogen atmosphere (circulation).

The crystallization of neat PLA and nucleated PLA was carried out two different procedures: The isothermal crystallization was performed in the temperature range of 90-130°C. The samples with a weight around 10 mg were put in an aluminum pan and hermetically sealed. The sample was first melted by heated it quickly from 25 to 200°C and maintaining it at 200°C for 5 min. Then, it was rapidly cooled to the isothermal crystallization temperature and held there until completion of crystallization (about 90 min). Once crystallized, the samples were heated to 200°C at a rate of 10°C/min in order to measure the melting endotherm. A nitrogen flow was maintained throughout the test.

For the non-isothermal crystallization, the samples were heated to 200°C and kept in the molten state for 2 min to erase the prior thermal history. They were then cooled at cooling rates of 5, 10, 20 and 30°C/min down to 25°C to evaluate their ability to crystallize upon cooling. Subsequently, the samples were heated back to 200°C at a rate of 10°C/min to assess the crystallization upon heating. The glass transition temperature (T_g), the cold crystallization temperature (T_{cc}), the degree of crystallinity (x_c), the degree of cold crystallinity (x_{cc}), and the melting temperature (T_m) were determined in the second heating scan. Based on the heat of fusion of 100% crystallinity of PLA (93 J/g), the degree of crystallinity or the degree of cold crystallinity of PLA was calculated from the melting endotherms of the samples and normalized with respect to the composition of each component in the plasticized PLA. The percent crystallinity was calculated using the following equation (1):

$$\% \, Cristallinity = 100 * \frac{\Delta Hm}{f \times \Delta Hm\infty} \tag{1}$$

Where ΔH_m is the measured heat of fusion, f is the weight fraction of the component in question and ΔH^{∞}_m is the enthalpy of fusion for a crystal having infinite crystal thickness ($93 J.g^{-1}$ for PLA).

RESULTS AND DISCUSSION

Non-Isothermal Crystallization Kinetics: Melting Behavior

The effect of nucleation on PLA's non-isothermal crystallization kinetics was investigated. Even though that a lower cooling rate is used, neat PLA exhibited no crystallization peak upon cooling and no significant crystallization endotherm upon heating (Figure **1**).

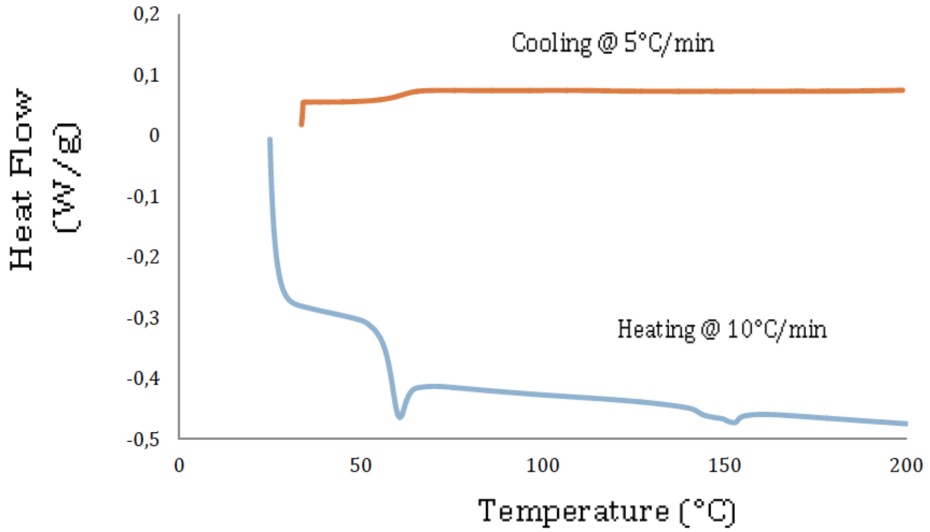
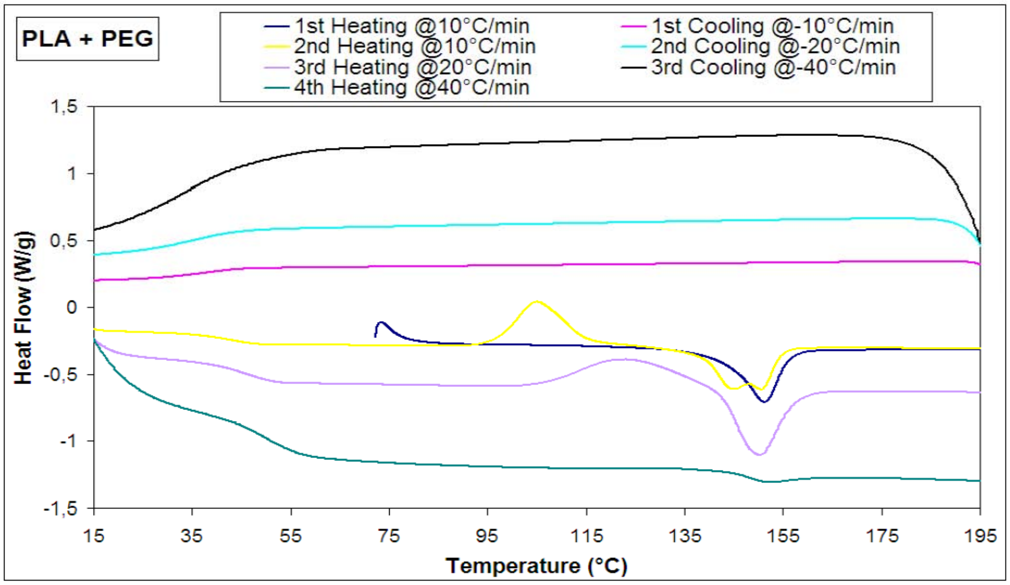


Figure 1: DSC thermogram of pure PLA after melting at 200°C (exo up).



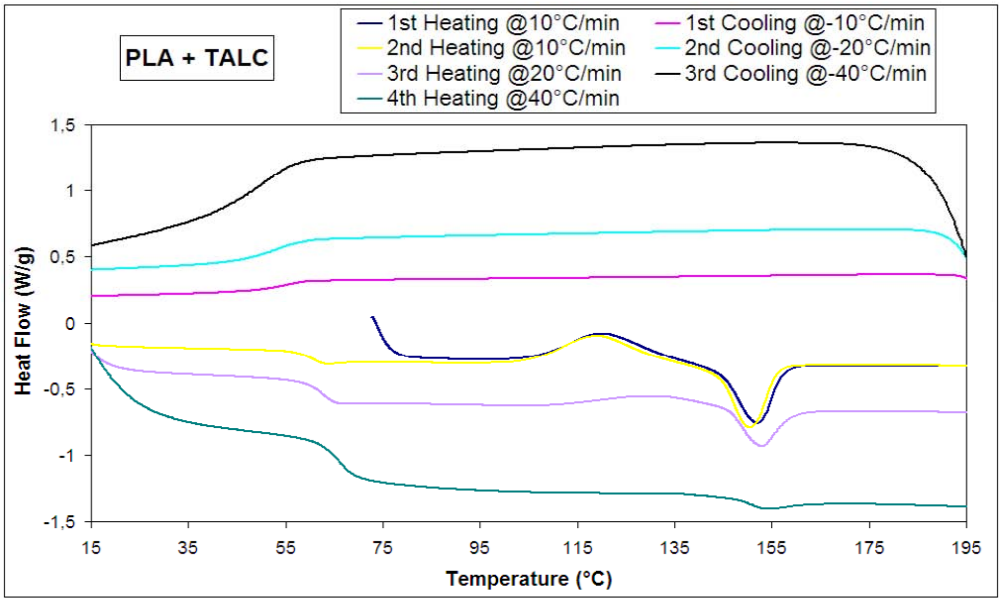


Figure 2: Result of DSC analysis – variation and influence of the heating rate.

The addition of talc and PEG at different heating rate (10, 20et 40°C/min) can also be observed in Figure **2** and **3**.

On the contrary, the addition of nucleating agents enhanced the formation of endothermic and exothermic peaks. Table **1** shows the values of crystallization temperature upon cooling (T_c) and upon heating (T_{cc}), enthalpy of crystallization (ΔH_c, ΔH_{cc}) and the degree of crystallization (X_c) for neat PLA and its blends. Only the pure PLA is very weakly crystallized because it presents a melting endotherm at 152.5°C with an enthalpy of 0.8 J/g in comparison to thermodynamical melting enthalpy of 94J/g for fully crystalline PLA. The addition of nucleating agents generates a crystallization peak upon cooling at a temperature range of 80- 125°C depending on the type of additive. A crystallization exotherm (cold crystallization) and a subsequent melting peak are observed for PLA/nucleating agent blends. At 1% nucleating agent loading, there is an increasing of the degree of crystallinity. This increasing is more pronounced when PLA was blended with talc, PEG and EBHSA together. As the EBHSA content was increased. The glass transition temperature of PLA is decreased with the presence of PEG.

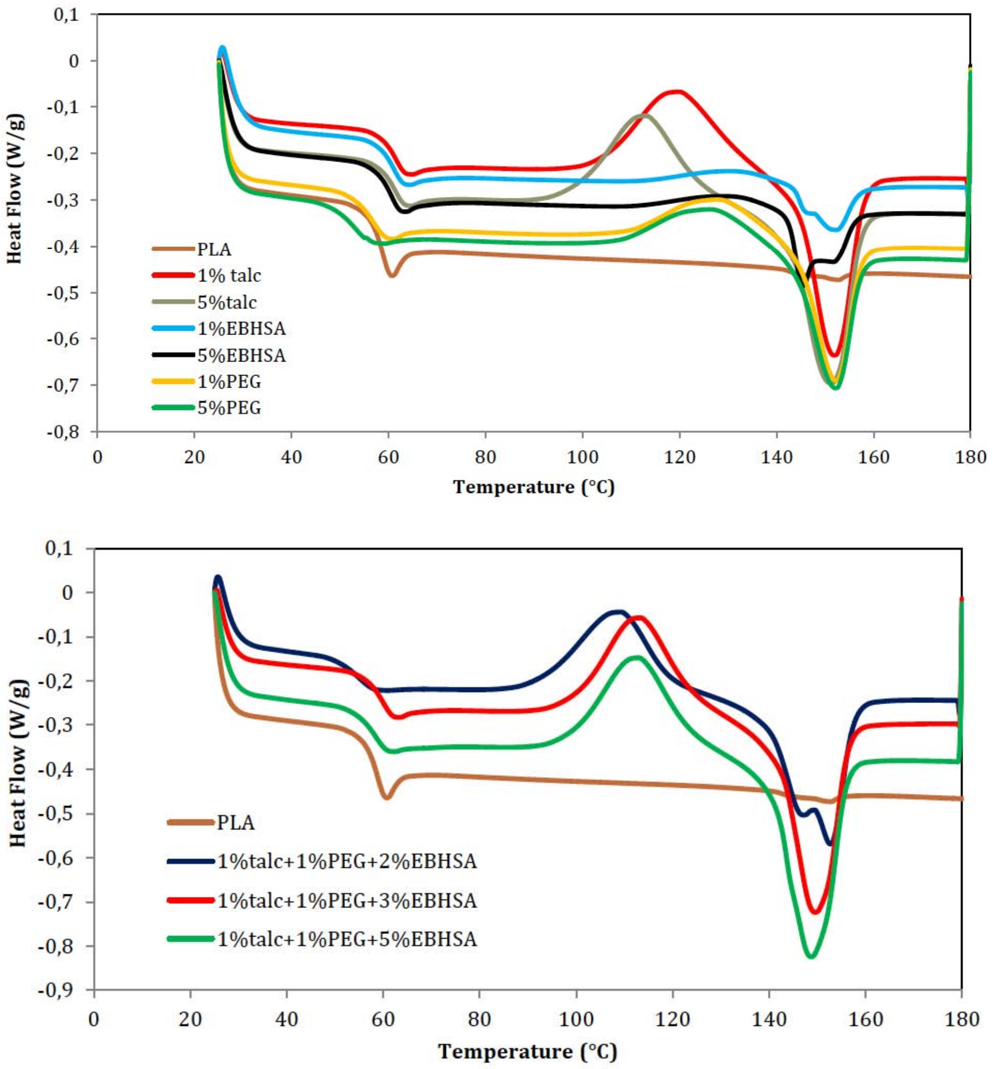


Figure 3: DSC melting thermograms of pure PLA and PLA/nucleating agents after cooling @5°C/min.

At 5% talc loading, a much sharper crystallization peak was observed upon cooling. The peak occurred at 89°C which is higher than that at 1% talc level.

EBHSA had limited effect on the PLA compared to others additives: a very weak and broad crystallization endotherm was found around 145-150°C. A small crystallization exothermic peak was observed prior to the major melting endothermic peak in the heating scans. This small exothermic peak was an additional crystallization that occurred at a higher temperature during the DSC-heating scan. A shoulder melting peak prior to the major melting peak appeared indicating two different type of growth of crystallites.

In the case of PEG, there is a decreasing of T_g which means the plasticization effect of PEG. As shown in the table, the blend of PLA with 1%wt of talc, 1%wt of PEG and 2%wt of EBHSA promotes an important crystallization of PLA. There is a discernible crystallization peak upon cooling at 86°C. However, a crystallization peak upon heating appeared at around 110°C showing that the increased chain mobility already increased slightly the ability of PLA chains to crystallize. This can be associated to two different phenomena. The first one is the increased chain mobility at low temperature associated with T_g depression. This reduction enables crystallization to happen upon heating at low temperatures. A second phenomenon is the formation of nuclei during the cooling process. They will increase the crystallization rate upon heating. Thus, the simultaneous use of a plasticizer (PEG) and an effective nucleating agent had a synergistic effect which significantly expanded the crystallization window by increasing the nucleation rate and increasing the chain mobility in the lower temperature range.

Table 1: Values of Glass transition temperature (Tg), Melting temperature (Tm), Crystallization Temperature (Tc), Cold Crystallization Temperature (Tcc), Fusion Enthalpy (ΔHm), Crystallization Enthalpy (ΔHc), Cold Crystallization Enthalpy (ΔHcc), Degree of Cristallinity (Xc)

	Blends PLA /nucleating agent	Tg (°C)	Tm (°C)	ΔHm (W /g)	Tc (°C)	ΔHc (W /g)	Tcc (°C)	ΔHcc (W /g)	Xc (%)
Neat PLA	100/0	57.2	152.5	0.8	101	0.3	------	------	0.86
PLA/talc	99/1	58.5	152	18.5	88.5	0.5	120	22.44	20
	95/5	58.2	151.2	21.2	89	2.1	113	19.3	24
PLA/EBHSA	99/1	58	151.6	4.8	125	1.35	131	2.9	5.2
	95/5	57.3	145.3	9.35	125	4.3	130	3	10.5
PLA/PEG	99/1	57.2	152	11.65	95.3	1.64	128.5	12.8	12.65
	95/5	48.7	152.4	11.1	93.5	1.9	127.4	16.46	12.5
PLA/talc/PEG/EBHSA	96/1/1/2	50.5	153	21.8	85.6	2.34	109.3	15.6	24.4
	95/1/1/3	56.5	149.6	24.6	87.7	0.74	113.4	22.6	27.8
	93/1/1/5	54.5	148.7	28.9	86.3	0.64	112.9	19.15	33.4

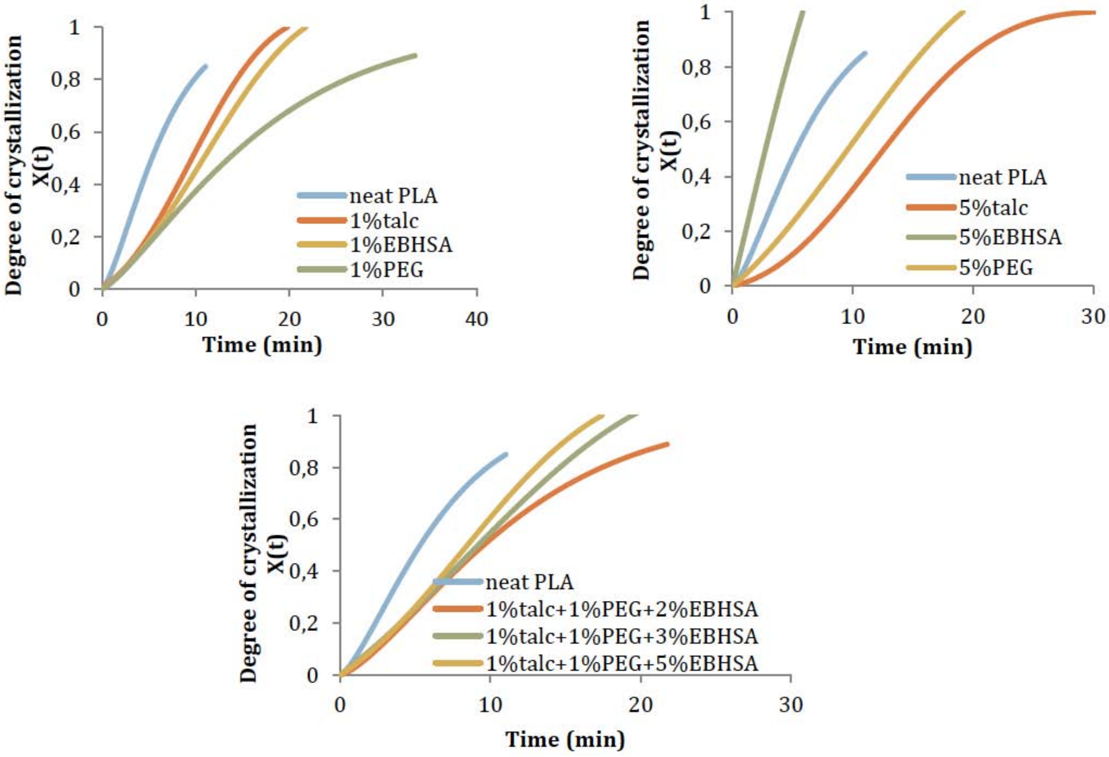


Figure 4: The relative degree of crystallization of PLA/nucleating agents as a function of the isothermal crystallization time.

Isothermal Crystallization Behavior

Typical crystallization isotherms, which were obtained by plotting the degree of crystallization X*(t)* versus *t* at optimum temperature T_{opt} are shown in Figure **4** for pure PLA and its blends with talc, PEG and EBHSA. This T_{opt} was determined from the temperature range of 85°C- 135°C. At T_{opt}, the maximum of crystallization was obtained.

For all the blends, except the only one with 5%EBHSA, the crystallization isotherm curves shifted along the time axis and followed the Avrami equation. At this optimum temperature, the half-time of crystallization (t ½), defined as the time required to reach 50% of the final crystallinity, decreased compared to neat PLA. This reduction should be confirmed by the effect of nucleation.

To sum up, we can find that EBHSA and PEG showed lower degree of crystallinity although the half-time of crystallinity (Table **2**). Thus, they were less efficient than talc and less efficient than the ternary blend of nucleating agent (talc/PEG/EBHSA).

The isothermal study at 90-100-105-110-120-130°C for PLA/PEG, PLA/talc and PLA/talc/PEG/EBHSA was obtained (Figure **5** and **6**).

The polarized light microscopy showed many different observations at different temperature 105-120

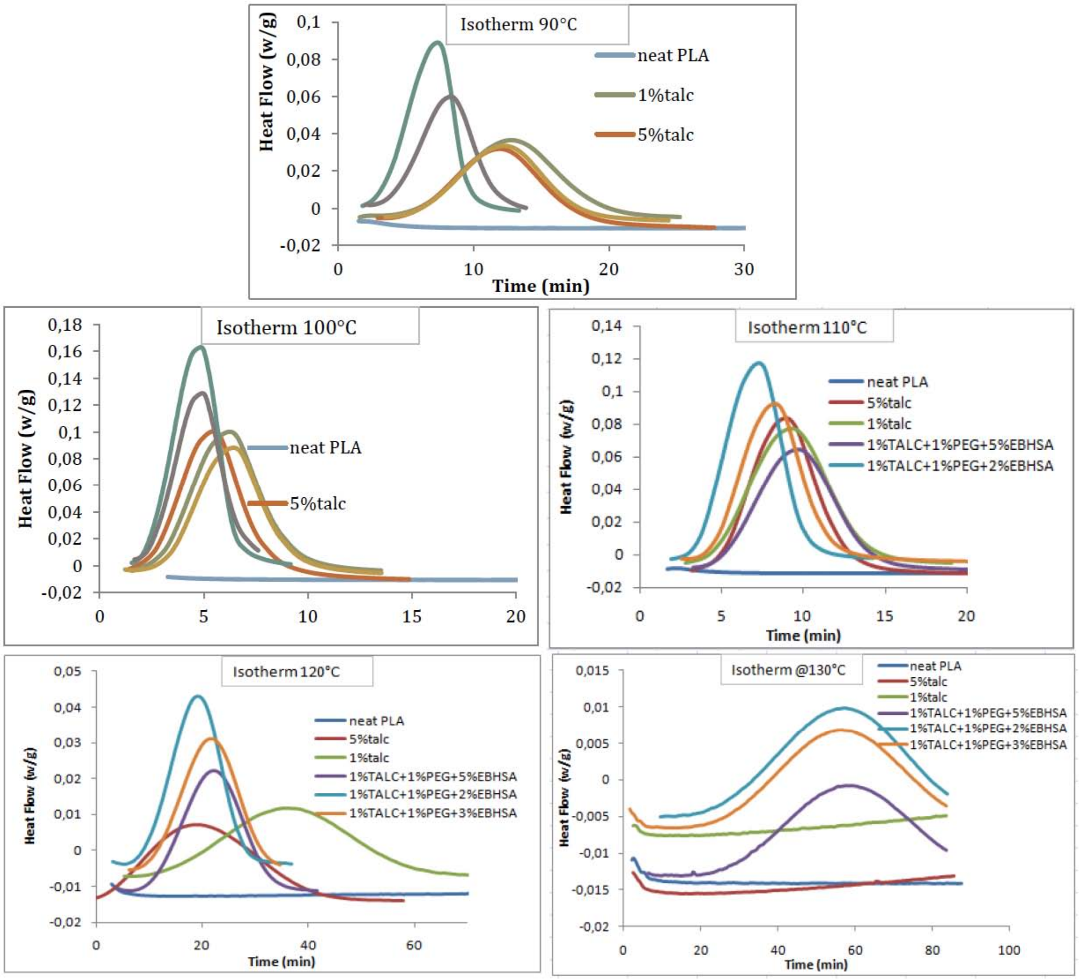


Figure 5: The Crystallization Enthalpy versus t at different isotherms of pure PLA and its blends.

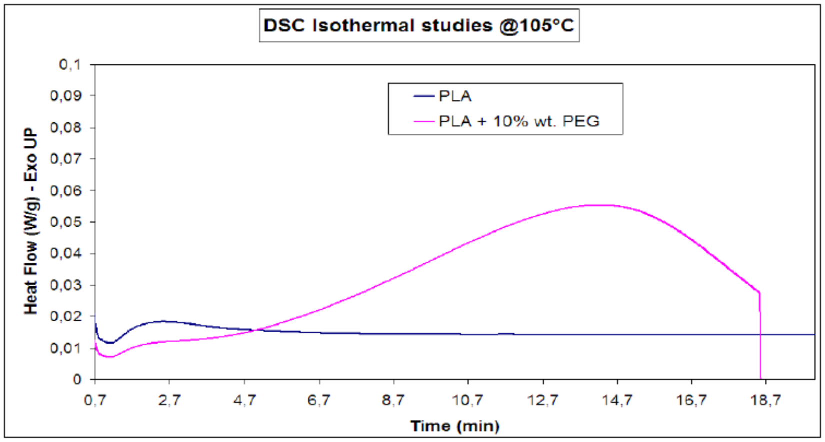


Figure 6: DSC results – Isotherm at 105°C.

et 125°C for PLA/PEG (10%) and PLA/TALC (1%) (Figure **7**).

By plotting the T_C against the half-time of crystallization (t ½), saddle shape curves for pure PLA and its blends with talc and ternary mixture were obtained. Absolute temperature units (K) were used for these plots according to the theory of isothermal crystallization kinetics. For PLA, the t ½ was around 30 minutes at temperature range of 90-130°C (363-403°K). The crystallization rates of these blends were faster than that of pure PLA (Figure **8** and **9**). Furthermore, as the talc content increased, the t ½ still unchanged at 363-373-383°K which is mean that at these temperatures, the crystallization rate of PLA was the same but decreased at 393°K (120°C), indicating that the crystallization rate of PLA was slightly increased. Talc is one of the most effective nucleating

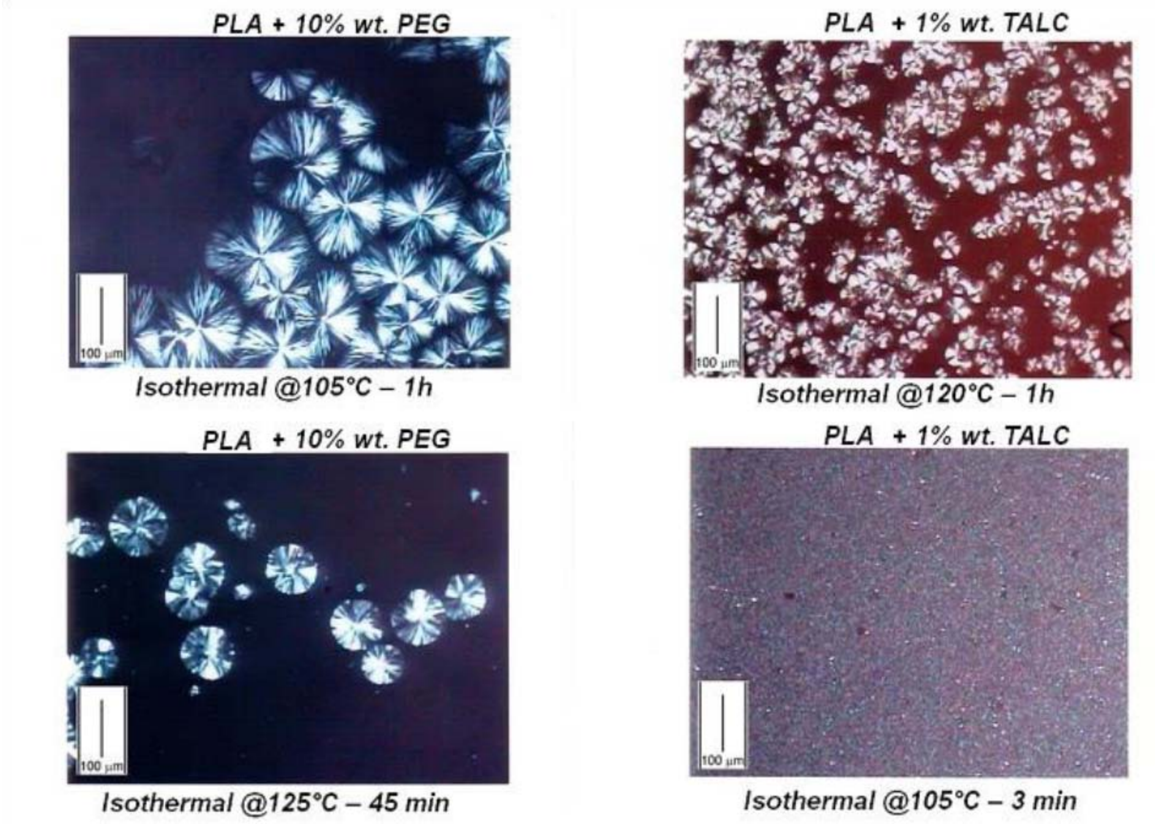


Figure 7: Polarized Light Microscopy Observation Before isothermal crystallization every samples were melted @200°C during 5 min.

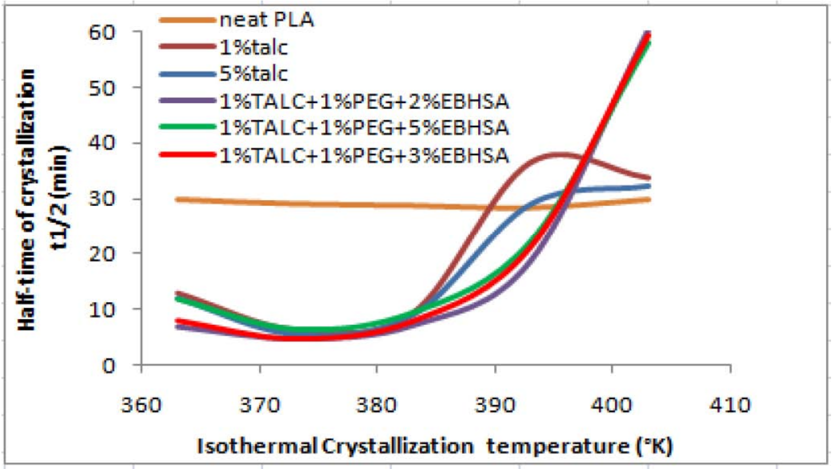


Figure 8: The half-time of crystallization (t1/2) as a function of the isothermal crystallization temperature (Tc) for pure PLA and its blends.

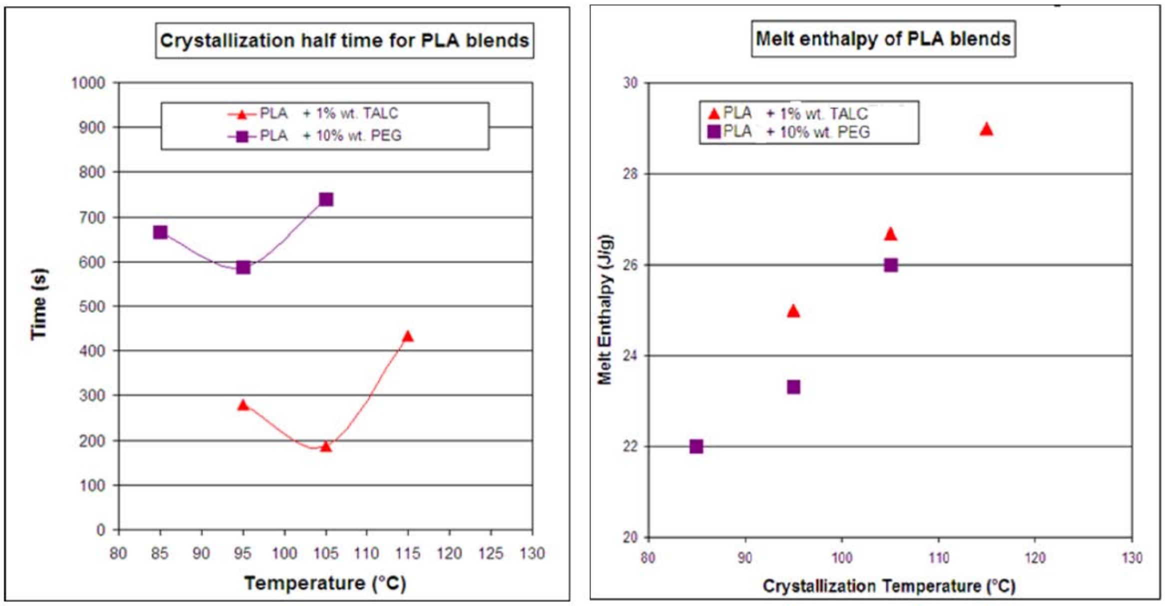


Figure 9: Determination of crystallisation half time with nucleant agents used independtly.

agents. The t ½ for the blend (PLA/talc/PEG/EBHSA) increased slightly as the content of EBHSA increased up 393°K. Above 393°K, t ½ decreased as EBHSA increased (Table **2**).

This showed that talc is a stronger nucleating agent in blends with PLA above 393°K (120°C) and the ternary mixture is stronger than talc below 393°K (120°C).

Table 2: The Values of $t_{1/2}$ at T_{opt} of PLA and its Blends

	Blend PLA /nucleating agent	Topt (°C)	t1/2 (min)
Neat PLA	100/0	105	26
PLA/talc	99/1	118	8.5
	95/5	119	11.2
PLA/EBHSA	99/1	119	9.6
	95/5	127	2.4
PLA/PEG	99/1	118	13.6
	95/5	118	8.5
PLA/talc/PEG/EBHSA	96/1/1/2	128	9.6
	95/1/1/3	130	7.6
	93/1/1/5	127	7.5

Figures **10** contain plots of ln[-ln(1-α)] versus ln t according to eq. for pure PLA and its blends with talc and talc/PEG/EBHSA, respectively. The experimental data fit the Avrami equation very well for the early part of the transformation and became slightly nonlinear toward the end. This was more evident in blends than in pure PLA. However, the Avrami method can still be used to roughly characterize the isothermal crystallization behavior of PLA and its blends.

From linear fitting of the Avrami equation, the values of K and n at different crystallization temperature for all samples were listed in Table **3**.

The Avrami exponent *n* differs from sample to sample, and it also various with T_c. The average *n* value in the T_c range tested was 2 for pure PLA; 4 for PLA/nucleating agents except PLA/talc at ratio 99/1. For PLA, the growth of crystallites was unidimensional homogeneous or Bidimensional heterogeneous and after adding nucleating agents, the crystallites were grow in a heterogeneous three-dimensional form. Besides, the n value is affected by many factors, such as the nucleation density.

CONCLUSION

A several studies have been carried out concerning the characterization, compounding and processing of bio based and biodegradables materials.Indeed, numerous investigations have been dedicated also to a (i) new formulation and (ii) processing of bio-based thermoplastic structure for packaging and medical application. The aim of the present work was firstly to give a pertinent ways to improve PLA's properties according to chosen process and final properties (for more details, cf. to our patent ([29]). Despite the

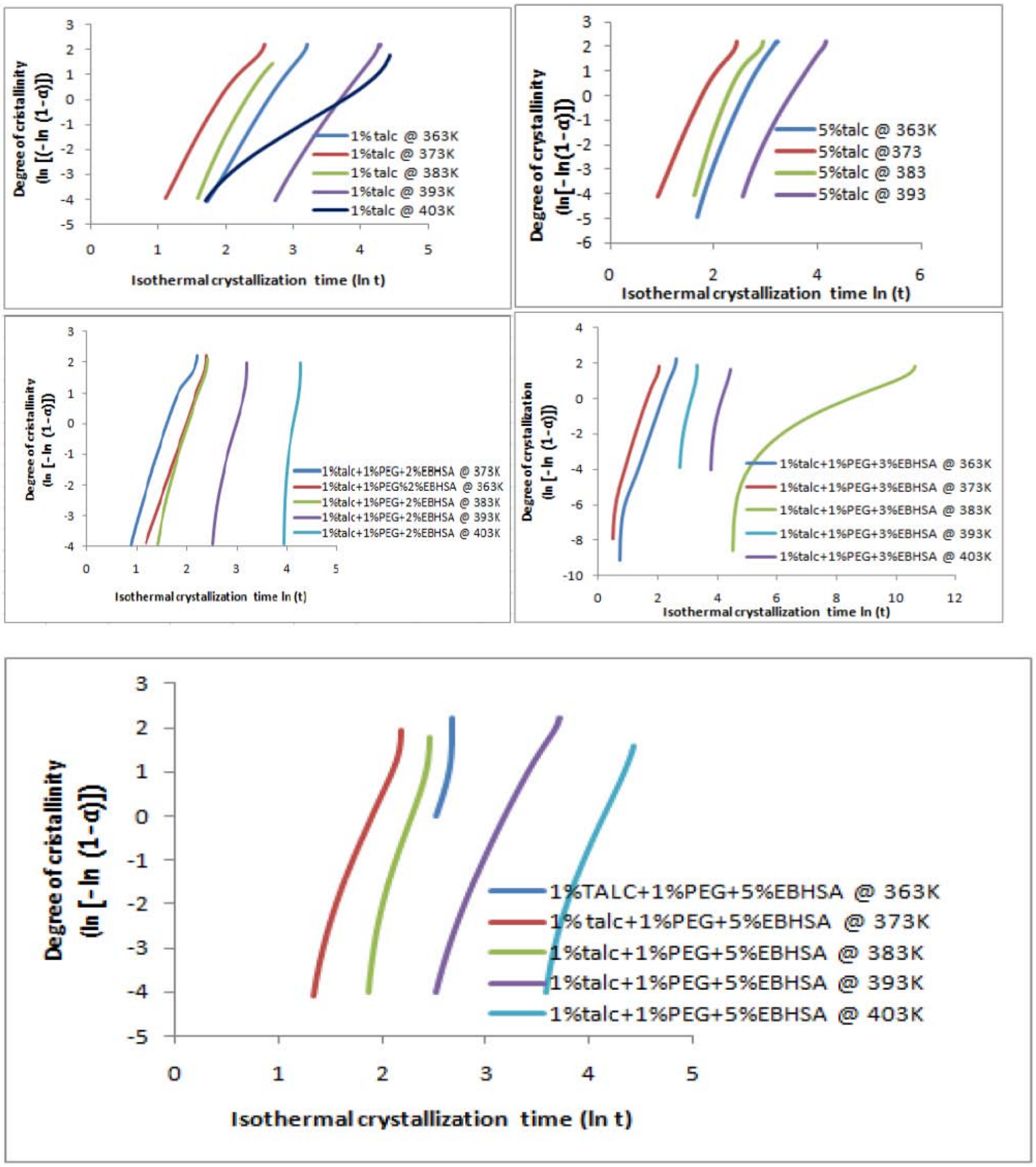


Figure 10: Plots of the degree of crystallization ln [-ln (1-α)] versus the crystallization time (ln(t) for isothermal crystallization of PLA and its blends.

interesting nature of the kind of research given in the literature, it is of no help when attempting to comprehend either how to enhance the physico-chemical, structural or processing properties of this interesting polymer in view of its proceessing. In order to attain these objectives, the attention of our work has been focused on performing original experiments to purpose a new way to improve PLA properties according to the different purposing route:

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 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.

3. 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 [29].

Table 3: Values of Overall Kinetic rate Constant (K) and Avrami Index (n) at Various Isothermal Crystallization Temperatures (Tc)

Blend PLA-nucleating agents	Tc (°K)	K (min^{-1})	n
PLA - 1% talc	363	$9,9*10^{-3}$	4,17
	373	$4,5*10^{-4}$	3,9
	383	$9,6*10^{-3}$	4
	393	$5,19*10^{3}$	3,8
	403	$1,2*10^{-3}$	1,8
PLA - 5% talc	363	$7,6*10^{-3}$	4,35
	373	$0,7*10^{-3}$	3,9
	383	$2,89*10^{2}$	4,29
	393	$8*10^{-3}$	3,5
PLA - 1% talc /1%PEG/2%EBHSA	363	$6,8*10^{-4}$	4
	373	$7,4*10^{-4}$	4
	383	$1*10^{-2}$	4
	393	$1,*10^{-4}$	4
	403	$2,4*10^{-4}$	4
PLA - 1% talc /1%PEG/3%EBHSA	363	$2,2*10^{-2}$	4
	373	$1,5*10^{-4}$	4
	383	$1,5*10^{-4}$	1
	393	$4,2*10^{-2}$	4
	403	$1,9*10^{-2}$	4
PLA - 1% talc /1%PEG/5%EBHSA	363	$5,7*10^{-2}$	4
	373	$2,4*10^{-2}$	4
	383	$6*10^{-4}$	4
	393	$1,8*10^{-3}$	4
	403	$5,7*10^{-2}$	4

To conclude, the crystallization behavior of PLA/nucleating agent's blends from the melt is influenced by the crystallization temperature and the composition. The results obtained indicate that the crystallization of PLA during heating from low temperatures was initiated by nuclei formed during the preceding cooling. Talc in PLA / talc blends can increase the crystallization rate of PLA. Another system as talc/PEG/EBHSA at ratio (1/1/2 or 1/1/3 or 1/1/5) can also be used as nucleating agent and the results showed that it was more effective than talc. It increased the degree of crystallinity (X_C), reduced drastically the half time of crystallization $t_{1/2}$ and accelerated the crystallization rate compared to neat industrial PLAs. The obtained results are with great interest for academy and industrial communities to coven different processing technologies ranging from Thermoforming to film extrusion or injection molding.

REFERENCES

[1] Tianyi Ke, Xiuzhi Sun, Journal of Applied Polymer science, 2003; 89; 1203-1210. https://doi.org/10.1002/app.12162

[2] R. Masirek, E. Piorkowska, A.Galeski, M.Mucha, Journal of Applied Polymer science, 2007; 105: 282-290. https://doi.org/10.1002/app.26047

[3] H. Li and M. Huneault, Polymer, 2007; 48: 6855-6866. https://doi.org/10.1016/j.polymer.2007.09.020

[4] Tuominen J, Kylmä J, Seppälä J. Chain extending of lactic acid oligomers. 2. Increase of molecular weight with 1,6-hexamethylene diisocyanate and 2,2'-bis(2-oxazoline). Polymer 2002; 43(1): 3-10. https://doi.org/10.1016/S0032-3861(01)00606-1

[5] Zhou ZF, Huang GQ, Xu WB, Ren FM. Chain extension and branching of poly (L-lactic acid) produced by reaction with a DGEBA-based epoxy resin. EXPRESS Polymer Letters 2007; 1(11): 734-739. https://doi.org/10.3144/expresspolymlett.2007.101

[6] Gruber PR, Hartmann MH, Kolstad JJ, Witzke DR, Brosch AL. 1996; PCT 94/ 08 508.

[7] Pilla S, Kim SG, Auer GK, Gong S, Park CB. Microcellular extrusion-foaming of polylactide with chain-extender. Polymer Engineering & Science 2009; 49(8): 1653-1660. https://doi.org/10.1002/pen.21385

[8] Yingwei D, Salvatore I, Ernesto Di M, Luigi N. Reactively Modified Poly (lactic acid): Properties and Foam Processing. Macromolecular Materials and Engineering 2005; 290(11): 1083-1090. https://doi.org/10.1002/mame.200500115

[9] Mihai M, Huneault MA, Favis BD. Rheology and extrusion foaming of chain-branched poly (lactic acid). Polymer Engineering & Science 2010; 50(3): 629-642. https://doi.org/10.1002/pen.21561

[10] Dorgan JR, Lehermeier H, Mang M. Thermal and Rheological Properties of Commercial- Grade Poly (Lactic Acid) Journal of Polymers and the Environment 2000; 8(1): 1-9. https://doi.org/10.1023/A:1010185910301

[11] Han Gi C, Byoung Chul K, Seung Soon I, Yang Kyoo H. Effect of molecular weight and branch structure on the crystallization and rheological properties of poly (butylene adipate). Polymer Engineering & Science 2001; 41(7): 1133-1139. https://doi.org/10.1002/pen.10814

[12] Krumme A, Lehtinen A, Viikna A. Crystallisation behaviour of high-density polyethylene blends with bimodal molar mass distribution 1. Basic characteristics and isothermal crystallisation. European Polymer Journal 2004; 40(2): 359-369. https://doi.org/10.1016/j.eurpolymj.2003.10.005

[13] Liu G, Zhao M. Isothermal crystallization kinetics of AB3 hyperbranched polymer (HBP)/polypropylene (PP) blends. Polymer Bulletin 2009; 63(4): 565-573. https://doi.org/10.1007/s00289-009-0128-x

[14] Mc Kee MG, Unal S, Wilkes GL, Long TE. Branched polyesters: recent advances in synthesis and performance. Progress in Polymer Science 2005; 30(5): 507-539. https://doi.org/10.1016/j.progpolymsci.2005.01.009

[15] Miyata T, Masuko T. Crystallization behaviour of poly(L-lactide). Polymer 1998; 39(22): 5515- 5521. https://doi.org/10.1016/S0032-3861(97)10203-8

[16] Al-Itry R, Lamnawar K., Maazouz A. 2014. Rheological, morphological, and interfacial properties of compatibilized PLA/PBAT blends Rheologica acta 53, 7, 501-517 DOI: 10.1007/s00397-014-0774-2. https://doi.org/10.1007/s00397-014-0774-2

[17] Walha F., Lamnawar K, Maazouz A. Jaziri M. Preparation and characterization of Bio-sourced Blends based on Poly (lactic acid) and Polyamide 11: Structure-properties relationships and Enhancement of film blowing processability. Advances in Polymer Technology 2018; 37 (6): 2061-2074. https://doi.org/10.1002/adv.21864

[18] Lamnawar K., Maazouz A., Cabrera G., Al-Itry R., Interfacial Tension Properties in Biopolymer Blends: From Deformed Drop Retraction Method (DDRM) to Shear and Elongation Rheology-Application to Blown Film Extrusion, International Polymer Processing Vol. 33, 3. 411-424 DOI 10.3139/217.3614

[19] Zenkiewicz M, Richert J, Rytlewski P, Moraczewski K, Stepczynska M, Karasiewicz T. Characterization of multi-extruded poly (lactic acid). Polymer Testing 2009; 28(4): 412-418. https://doi.org/10.1016/j.polymertesting.2009.01.012

[20] Wang Y, Steinhoff B, Brinkmann C, Alig I. In-line monitoring of the thermal degradation of poly (l-lactic acid) during melt extrusion by UV-vis spectroscopy. Polymer 2008; 49(5): 1257-1265. https://doi.org/10.1016/j.polymer.2008.01.010

[21] Bopp RCGV, MN, US), Whelan, Jason (New Hope, MN, US). 2008(20080258357).

[22] Van den Oever MJA, Beck B, Müssig J. Agrofibre reinforced poly (lactic acid) composites: Effect of Moisture on degradation and Mechanical properties. Composites Part A: Applied Science and Manufacturing.In Press, Accepted Manuscript. 2010.

[23] Shin S, Kazuhiko I, Masatoshi I. Development of Kenaf Fiber-Reinforced Polylactic Acid for Use in Electronic Products. Japanese Journal of Polymer Science and Technology 2005; 62(4): 177-182.

[24] Xu H, Teng C, Yu M. Improvements of thermal property and crystallization behavior of PLLA based multiblock copolymer by forming stereocomplex with PDLA oligomer. Polymer 2006; 47(11): 3922-3928. https://doi.org/10.1016/j.polymer.2006.03.090

[25] Anderson KS, Hillmyer MA. Melt preparation and nucleation efficiency of polylactide stereocomplex crystallites. Polymer 2006; 47(6): 2030-2035. https://doi.org/10.1016/j.polymer.2006.01.062

[26] Iotti M, Fabbri P, Messori M, Pilati F, Fava P. Organic–Inorganic Hybrid Coatings for the Modification of Barrier Properties of Poly (lactic acid) Films for Food Packaging Applications. Journal of Polymers and the Environment 2009; 17(1): 10-19. https://doi.org/10.1007/s10924-009-0120-4

[27] Hirvikorpi T, Vähä-Nissi M, Harlin A, Karppinen M. Comparison of some coating techniques to fabricate barrier layers on packaging materials. Thin Solid Films 2010; 518(19): 5463-5466. https://doi.org/10.1016/j.tsf.2010.04.018

[28] Sinha Ray S, Okamoto K, Okamoto M. Structure - Property Relationship in Biodegradable Poly (butylene succinate)/Layered Silicate Nanocomposites. Macromolecules 2003; 36(7): 2355- 2367. https://doi.org/10.1021/ma021728y

[29] Maazouz A., Lamnawar K., Mallet B. 2010. Polymer composition based on poly lactic acid, useful in piece/object, comprises poly lactic acid and additive mixture, for promoting crystallization of poly lactic acid, comprising mineral filler, glycol polyether, and aliphatic amide. Accepted French and International patent: C08L67/00; C08J5/10. FR2941702 (A1);

[30] Maazouz A., Lamnawar K., Mallet B. Frontiers in Science and Engineering (international journal) 2011: 1-44.

[31] Walha F., Lamnawar K., Maazouz A, Jaziri M. Rheological, Morphological and Mechanical Studies of Sustainably Sourced Polymer Blends Based on Poly (Lactic Acid) and Polyamide 11. Polymers 2016; 8(61): 1-23. https://doi.org/10.3390/polym8030061

[32] Al-Itry R., Lamnawar K., Maazouz A. Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy, Polymer Degradation and Stability 2012; 97(10): 1898-1914. https://doi.org/10.1016/j.polymdegradstab.2012.06.028

Received on 15-12-2018 Accepted on 27-12-2018 Published on 31-12-2018

DOI: https://doi.org/10.12974/2311-8717.2018.06.5