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A review on thermal degradation of polylactic acid (PLA)/polyhydroxybutyrate (PHB) blends

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Abstract:

Poly(lactic acid) (PLA) and poly(hydroxybutyrate) (PHB) are two biopolyesters produced from renewable resources like corn or sugar followed by bacterial fermentation. PLA is the most widely used biopolymer in diverse applications. Addition of PHB to PLA can improve PLA's crystallinity and thereby its mechanical properties. However, both PLA and PHB suffer from poor thermal stability, which limits their potential industrial application. The purpose of this review is to explain the thermal decomposition mechanism of these polymers and summarize reports on the thermal degradation of neat PLA and PHB, PLA/PHB blends and PLA/PHB blends modified/reinforced with plasticizers, additives or crosslinkers. The characteristic temperatures (T_{onset} , T_{max}) of PLA and PHB are taken as key parameters to evaluate PLA/PHB blends and composites with variable composition. From this review we conclude that the thermal stability of PLA in PLA/PHB blend is lower than neat PLA, contrary to PHB with higher thermal stability in PLA/PHB blend. Moreover, the selection of additive severely affects the thermal stability of PLA/PHB blends. Processing method and localization of additive in different phases in or at the interface of the blend are recognized as determining factors in this regard.

Keywords: Thermal degradation; Poly(lactic acid); Poly(hydroxybutyrate); Polymer blends; Thermogravimetric analysis

1. Introduction

It is impossible to imagine our world without polymers. They are key materials in our daily life and due to providing good properties and flexibility to processing, resistance to chemicals and corrosive environment and also their reasonable price compared to metals, they are

produced 368 millions of tons worldwide [1]. Plastics are mainly used in automotive [2], [3], water purification [4], aeronautics [5], [6], packaging [7], [8] and biomedical [9], [10] fields. Despite their appropriate mechanical properties, conventional non-biodegradable polymers are not environmental-friendly [11]. Thus, synthesis and application of biodegradable polymers has become a necessity nowadays. Polylactic acid (PLA) is the most widely used biopolymer, known as the first generation biobased biodegradable polyester, which is derived from renewable resources such as corn starch and sugar [12]. Lactic acid, the monomer of PLA, exists in two optical isomeric forms: isomer L (Levorotary) and isomer D (Dexorotary), such that the resulting polymers are named PLLA and PDLA, respectively [13]. PLA has been widely used in packaging and biomedical fields due to its biocompatible and bioresorbable properties [14], [15]. The use of PLA for food packaging applications is pertinent to modification. PLA is a rigid and brittle material with poor barrier properties. Therefore,, different green polymers such as poly(butylene succinate) (PBS) [16], chitosan [17] and thermoplastic starch (TPS) [18] have been blended with PLA to improve its mechanical strength for packaging and biomedical applications.

Since PLA is mainly obtained from corn, there was a need for finding an alternative in order to protect agricultural resources. Polyhydroxyalkanoates (PHAs) are second generation of biodegradable polyesters obtained through bacterial fermentation [19]–[21]. Polyhydroxybutyrate (PHB) is the most famous member of this family, a highly-crystalline biobased biodegradable polyester, which gives properties of thermoplasticity and biodegradability, but has poor thermal stability [20]. Thus, some believed that PLA and PHB are complements to each other. Correspondingly, there has been an ascending trend in the number of reports on PLA/PHB blends (Figure 1). Typically, PHB compensates for the low crystallinity of PLA and therefore, boosts the barrier properties of PLA [22], [23] required for food packaging applications. Unlike PLA, which is biodegradable in industrial composters, PHB is biodegradable under normal conditions [24], [25]. Therefore, addition of PHB to PLA increases the biodegradability of PLA. Despite having quite similar chemical structures, PLA and PHB are not miscible, which deteriorates the mechanical properties of their blend. Critically, thermal stability of PHB is poor, ending in thermal degradation in the vicinity of its melting point [24]. Thus, it is of importance to study thermal degradation mechanism of PLA, PHB and their blends.

In line with increasing demand for PLA/PHB blends, investigations on their thermal properties are becoming more interesting. In this regard, some attempted to improve the

thermal stability of PLA/PHB blends . For example, incorporation of plasticizers [26]–[28] and reinforcement fillers [29]–[31] are two major strategies used for the improvement of processing and thermomechanical properties of PLA and PHB. There has also been some serial publications on the biodegradation of PLA/PHB blends [32]–[34]. In this review, we overviewed thermal degradation of PLA, PHB, their blends, and composites containing additives/fillers , thermally and mechanically. We also reviewed and explained techniques used in making PLA/PHB cross-linked, as well as their chemistry and mechanisms underlying thermal degradation. Moreover, dependency of thermal stability on the composition of PLA/PHB blends was particularly discussed. Challenging aspects of future developments on thermally stable PLA/PHB blends were highlighted.

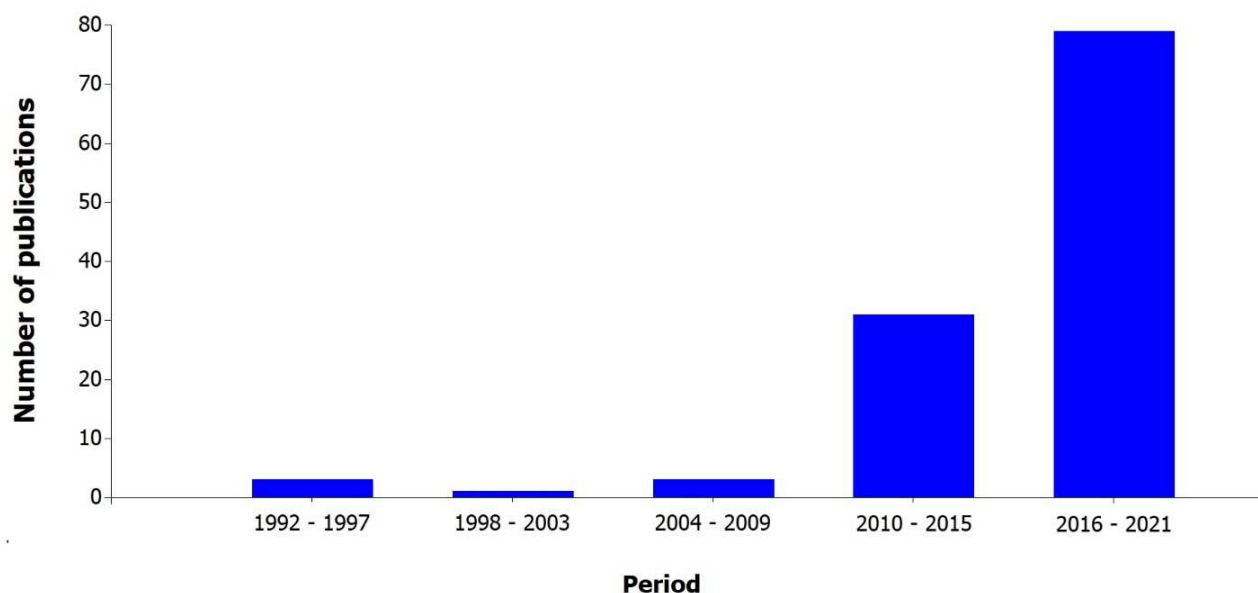


Figure 1: Number of publications per year on PLA/PHB blends (data from sciencedirect and google scholar, keyword: PLA/PHB blend). It is apparent from data that the number of publication on PLA/PHB blends increased abruptly since 2010.

2. Thermal stability of PLA, PHB, and PLA/PHB blends

2.1 Thermal decomposition of neat PLA

According to the results obtained in thermogravimetric analysis (TGA), thermal decomposition of PLA starts around 200 °C [35]. During an isothermal TGA analysis at 200 °C, Arrieta *et al.* [36] observed no significant mass loss for PLA after 20 min. The mass loss

was approximately 1 wt.% after 20 min at 200 °C, which indicated that PLA could be processed at 200 °C without a significant degradation. Generally, PLA degrades in one step around 350 °C [37]–[39]. However, in some cases two degradation steps have been reported, at 300 °C and 340–360 °C [40]. This difference could be explained by the complexity of the thermal degradation of the PLA or the chemical structure in terms of stereoisomerism of the polymer [35]. The stereoisomerism of PLA due to the presence of L or D isomers can influence the thermal properties of the polymer. Tsuji *et al.* [41] compared the thermal properties of poly(L-lactic acid) (PLLA), poly(D-lactic acid) (PDLA) and equimolar PLLA/PDLA blend. They observed that the mass loss curve of the PLLA/PDLA blend was situated between those of virgin PLLA and PDLA, but resulted in a higher final residue weight percentage for the blend. After 350°C the mass of PLLA/PDLA blend was higher than L and D films, probably due to the entanglement of chains. The isothermal TGA analysis showed a higher mass loss for PLLA and PDLA than their blend. During the non-isothermal TGA analysis, the mixed L/D film showed mean mass loss behavior between those of the neat L and D films, and a lower degradation temperature, but a higher amount of mass residue. They concluded that the blend with 50 wt% of PLLA and 50 wt% of PDLA was more thermally stable and the improvement of the thermal stability came from the strong interactions between the chains of PLLA and PDLA. The TGA analysis performed by Varol [42] showed that the PLLA pellets degrade at 296 °C, while the PDLA pellets degrade at 321 °C. This difference can be explained by the molecular weight of the two PLA. The number average molecular weight of PLLA and PDLA were respectively 53 kDa and 56kDa. The maximum degradation peak on the derivative curves (T_{max}) showed much less temperature variation between the homopolymers with 5 °C difference. PLLA/PDLA blends with a ratio w/w 50:50 were done by solvent casting method and extrusion. When the stereocomplex was done by extrusion this degradation was initiated before 300 °C while PLLA and PDLA homopolymers degraded after 300 °C. The hypothesis was a partial degradation of polymer chains during extrusion. When the stereocomplex was done by solvent casting method no significant change was observed between the thermal stability of PLLA, PDLA and the blend PLLA/PDLA. The blend had a lower temperature for 50% mass loss than the neat PLLA and neat PDLA, but higher T_{max} [42]. Park *et al.* [43] observed the decomposition of neat PLLA and neat PDLA in the vicinity of 250 °C and the decomposition temperature of PLLA/PDLA blends with different ratios close to 300 °C. The addition of PDLA in PLLA limitedly increased the onset decomposition temperature. The thermal stability of the blend slightly

increased when the amount of PDLA increased. This improvement in the thermal stability could be explained by a higher entanglement of chains which decreased the mobility of the chains and increased the thermal stability. The thermal stability of PLA was affected by stereoisomerism. In addition, due to a denser chain packing, a PDLA/PLLA mixture containing both isomers could principally be expected to be more stable than PDLA or PLLA. To limit thermal degradation of PLA, one can make use of thermal oxidation stabilizers. Oliveira *et al.* controlled thermal-mechanical degradation of PLA during multiple cycles of processing with B900, a primary and secondary antioxidant which limited the chain scission of PLA chains [44]. Masek and Latos-Brozio [45] explained the potential of flavonoids to stabilize PLA against oxidation, which results from hydroxyl groups present in the flavonoids. Amaro *et al.* [46] monitored thermal oxidation of PLA under the influence of intercalated double hydroxides used as antioxidant. Some grafted phosphite functional polysilsesquioxane on PLA chains to protect PLA against thermal oxidation and preserved the molecular weight [47].

2.2 Thermal decomposition of PHB

Since the degradation temperature of PHB is closed to its melting point, there are some serious drawbacks in its industrial development because of its small processing window, which can lead to the degradation of the polymers during the process. TGA analysis of PHB synthesized in laboratory scale showed that it degrades in one step between 220 and 290 °C, (Table 1). However, in the case of commercial PHB, two mass losses can be observed at 295 °C and 402 °C [48]. Indeed, commercially available PHB generally contains small amounts of additives such as polybutyladipate (PBA) or talc [49], and the degradation of these additives are simultaneously observed [48]. To explain this low thermal stability, Lee *et al.* [50] reported a complete degradation of PHB after 10 min at 250 °C by isothermal TGA analysis.

Kawalec *et al.* [51] investigated the thermal degradation of PHB samples with different molecular weight, microstructure and terminal groups. The comparison between two samples with the same molecular weight but with carboxylate for one and carboxylic for the other as terminal group showed an important decrease in T_{max} from 289 °C to 225 °C when the terminal group was a carboxylate salt. No significant change was observed when the molecular weight changed in the case of the sample with carboxylic acid as terminal group, but with carboxylate salt the T_{max} value decreased from 252 °C to 227 °C. Correspondingly,

the molecular weight was decreased from 36000 g.mol⁻¹ to 5600 g.mol⁻¹. This decrease could be explained by a higher amount of carboxylate salt moieties when the molecular weight was lower. Moreover, no significant evolution of the T_{max} was noticed for the samples with atactic or isotactic structure for each terminal group. PHB with carboxylate salt as terminal group showed an increase of the T_{max} when the amount of carboxylate salt in the polymer was decreased. Tocháček *et al.* [52] investigated the effect of thermooxidation stabilizers on PHB degradation behavior. Five groups of stabilizers with different mechanisms were studied: (i) sterically hindered phenols, which eliminate the alkylperoxyl radicals, (ii) organic phosphites, which react with hydroperoxydes, alkoxy and alkylperoxyl radicals, (iii) amines light stabilizers (HALS), which react with C-centered, alkoxy and alkylperoxyl radicals, (iv) carbodiimide, which react with hydrolytic scission intermediate and others stabilizers like aminoxide, and (v) hydroxylamine or lactone, which react with C-centered radicals. They concluded that common primary and secondary antioxidants and HALS are not effective. Such a behavior was interpreted in terms of a particular type of mechanism of action, which was indicative of no radical scission during the extrusion of PHB at 180-190°C. In conclusion, no commonly used stabilizer was able to protect the PHB during processing, but in some cases could limitedly avoid thermal degradation to some extent.

Thermal degradation of PHB could be governed by its chemical composition, particularly the end group moieties. In the case of carboxylate salt as terminal group, the molecular weight was also effective. The tacticity of PHB has no effect on the thermal stability of the polymer.

Table 1 summarizes characteristics including as molecular weight, L/D ratio, and density or MFI of the PLA and PHB for some commercial grades, together with thermal properties of these polymers obtained from TGA analysis.

Table 1: References of polymers (Ref polymer), Melt Flow Index (MFI), percentage of enantiomer L and D in the blend (L/D), molecular weight of the polymers, polydispersity (D), density, Tonset, , information and characteristic temperatures of neat PLA and neat PHB, Tonset, Tmax and the residue amount at the end (Residue) (^a : Tonset = temperature for 5% mass loss; ^b : Tonset = temperature the onset degradation; ^c : TGA at 20°C/min, Tmax = Temperature at the maximum rate obtained from the first derivative of TGA curve).

Polymer	Ref polymer	MFI (g/10min)	L (%) / D (%)	Molecular weight (g.mol ⁻¹)	D	Density (g.cm ⁻³)	T _{onset} (°C)	T _{max} (°C)	Residue (%)	Refs.
PLA	4032D, Naturworks	7 (210 °C, 2.16 kg)	98/2	52 000 (Mol weight)	1.9	1.24	324	357	0.12	[38]
	4042D, Naturworks	4 – 8 (210 °C, 2.16 kg)	92/8	211 332 (Mw)	2	1.24	251.3	327.4	NA	[53]
	3051D, Naturworks	7.75 (210 °C, 2.16 kg)	96/4	14 200 (Mn)	NA	1.25	NA	361	NA	[39], [54]
	4032, NatureWorks	7 (210 °C, 2.16 kg)	98/2	52 000	1.80	1.24	387.46/390.65	NA	1.51 – 4.78	[55]
	7001D, NatureWorks	6		110 100	1.59	1.24				
	PLA, NatureWorks	NA	NA	88 500 (Mn)	NA	NA	NA	282.56	NA	[56]
	Ingeo Biopolymer 3100HP, NatureWorks	24 (210 °C, 2.16 kg)	NA	148 250 (Mw)	1.81	1.24	NA	347	1	[37]
	PURAPOL L100IXS, Corbion Purac	20 -25 (190 °C, 2.16 kg)	NA	NA	NA	NA	NA	370	0.9	[57] ^c
2003D, NatureWorks	6 (210 °C, 2.16 kg)	96-95/4-5	156 000 (Mn)	NA	1.24	322	363	NA	[58] ^a	

	2002D, NatureWorks	5 – 7 (210 °C, 2.16 kg)	96/4	98 000 (Mn)	1.46	NA	320	357	NA	[36] ^a
	Ingeo 4032D, NatureWorks	7 (210 °C, 2.16 kg)	98/2	217 000	2	1.24	315	366	NA	[27] ^b
	PLLA Lacty 5000, Shimadzu Co.	NA	95/5	440000 (Mw)	2.1	NA	NA	NA	NA	[41]
	2003D, NatureWorks	6 (210 °C, 2.16 kg)	96/4	98 000	NA	1.24	315.7	345.5	NA	[28]
	4043D, NatureWorks LLC	6 (210 °C, 2.16 kg)	95.7/4.3	390 000 (Mw)	NA	1.24	NA	NA	NA	[59]
	4032D, NatureWorks LLC	7 (210 °C, 2.16 kg)	98.6/1.4	52 000	1.80	1.25	NA	NA	NA	[29]
PHB	Biocycle, PHB Industrial	NA	NA	425 000	2.51	NA	NA	279	0.25	[38]
	P226, Biomer	9 – 13 (190 °C, 1.16 kg)	NA	426 000	NA	1.25	223.4	NA	NA	[53]
	PHB, NaturPlast	15 – 30 (190 °C, 2.16 kg)	NA	NA	NA	1.25	NA	NA	NA	[39], [54]
	PHB, Ningbo Tianan Biologic Mat.	8-15 (210 °C, 2.16 kg)	NA	NA	NA	1.25	282.56	NA	6.56	[55]
	PHB, Industrial SA.	NA	NA	246 000 (Mn)	NA	NA	NA	306	NA	[56]
	BU396311, GoodFellow	10	NA	550 000	NA	NA	NA	272	2	[37]

	Inc.									
	P226, Biomer	9 – 13 (190 °C, 1.16 kg)	NA	426 000	NA	1.25	NA	302	1.2	[57] ^c
	BRS Bulk Bio-Pellets, Golden Valley Mn	NA	NA	190 000 (Mw)	NA	NA	290	NA	NA	[59]
	PHB, Ningbo Tianan Biologic Mat.	NA	NA	110 200 (Mn)	1.4	NA	219	255	NA	[58] ^a
	PHI002, NaturPlast	15-30 (190 °C, 1.16 kg)	NA	NA	NA	1.25	NA	NA	NA	[36]
	P226, Biomer	9 – 13 (190 °C, 1.16 kg)	NA	426 000 (Mw)	NA	1.25	NA	NA	NA	[27]
	PHB powder, Biomer	NA	NA	NA	NA	NA	NA	NA	NA	[29]
	PHB, GoodFellow	NA	NA	NA	NA	NA	NA	295	2.2	[48]
	PHB, Biomer	NA	NA	NA	NA	NA	NA	NA	0.5	[60]
	P226, biomer	10 (180 °C, 5 kg)	NA	426 000	NA	1.25	NA	272.3	NA	[61]

2.3 Thermal stability of PLA/PHB blends

Several investigations have been carried out on PLA/PHB blends in order to improve some properties of PLA such as biodegradability, crystallinity index or mechanical properties for applications in the field of packaging. The thermal stability of PLA/PHB blends with various composition have been studied and reported in Table 2. No significant mass loss was observed for each polymer during isothermal TGA analysis at 180 °C, which indicated that these polymers could be processed at this temperature without a risk of degradation [27], [62]. The TGA curves of the PLA/PHB blends during a dynamic analysis revealed a two-stage degradation for the blends. The first step of mass loss was attributed to the degradation of PHB, while the second one was related to PLA [37], [58]. As already explained, the difference between the degradation temperatures of PLA and PHB (Table 2) is due to the thermal stability of PLA, which is higher than that of PHB. Lai *et al.* [58] noted a decrease in T_{\max} of PLA in PLA/PHB blends. In agreement with other studies, they concluded that the addition of PHB to PLA suppresses thermal stability of PLA, Figure 3 [39], [54], [55]. On the other hand, the T_{\max} of PHB in the blend was greater than that of neat PHB for the ratios of 95/05, 90/10, 85/15 and 80/20, with respectively an increase of 33 °C, 27 °C, 23 °C and 19 °C for PHB, Figure 2 [58]. These conclusions on the thermal stability of PLA and PHB were also confirmed for lower ratios in PLA as 75/25 [38] or 70/30 [53], [59]. Cárdenas-Triviño *et al.* [55] suggested the hypothesis of a possible interaction and positive effect for a PLA/PHB 70/30 blend with three degradation steps observed on the TGA curve of the blend. Two steps corresponded to the PHB (284 °C) and PLA (341 °C) and an intermediate step (300 °C) with very low mass loss. This synergistic effect was similarly reported by Zhang and Thomas [23] with an improvement in the mechanical properties of 75/25 w/w/ PLA/PHB blend. They suggested that with this ratio, the transesterification between the chains of PHB and PLA can improve the properties of the blend.

Figure 3 shows variation T_{\max} of PLA when blended with PHB, extracted from the literature. The results of the study of Lai *et al.* [58] showed an increase in the T_{\max} of PLA in the blend when the amount of PLA increases. It may be due to a higher thermal stability of the PLA, which improves the thermal stability of the blend. Moreover, for the same ratio, several values of T_{\max} were observed. For example, for 70/30 PLA/PHB composition, two values of T_{\max} were obtained with a difference of 50 °C. In this study all experimental parameters were similar excepted the PLA used and TGA program. The higher values [57] were resulting from a program with heating rate of 20 °C/min, whereas the second study [53] used a heating rate

of 10 °C/min. When the heating rate increases, the curves of TGA shift toward higher temperatures, which can explain this difference between the T_{max} values obtained [63]. For the ratio 75/25, the values of T_{max} are in a range between 334 and 363 °C. This difference can be due to the method used to realize the blends. The higher values of the T_{max} with PLA amount increase were obtained by Frone *et al.* [29] for solvent casting blends. Contrary to the melting method, the solvent casting method does not work at high temperature; therefore, there is no thermal degradation of the polymer during the process. This can explain the higher value for the solvent casting method. The lower value was obtained by Arrieta *et al.* [64] by electrospinning. The other blends realized by extrusion had higher values between 350 °C and 370 °C. As a result, when PLA and PHB blended, the thermal stability of PHB increased, but the thermal stability of PLA decreased. This behavior was the case regardless of the ratio of PLA/PHB in the blend.

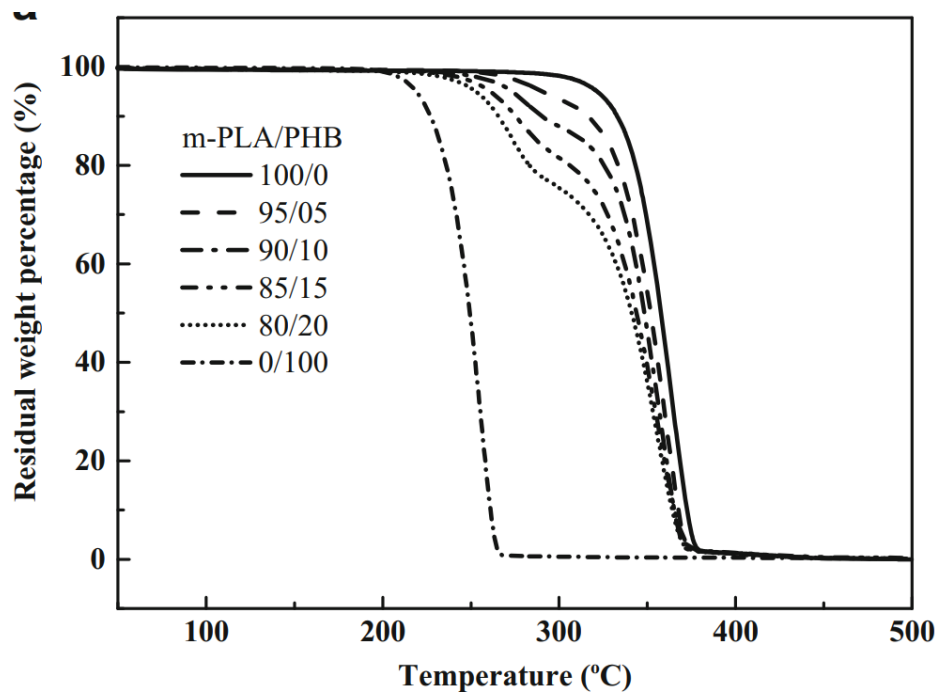


Figure 2: Typical of TGA of PLA/PHB blends by Lai *et al.*[58] (Copyright 2022, Elsevier).

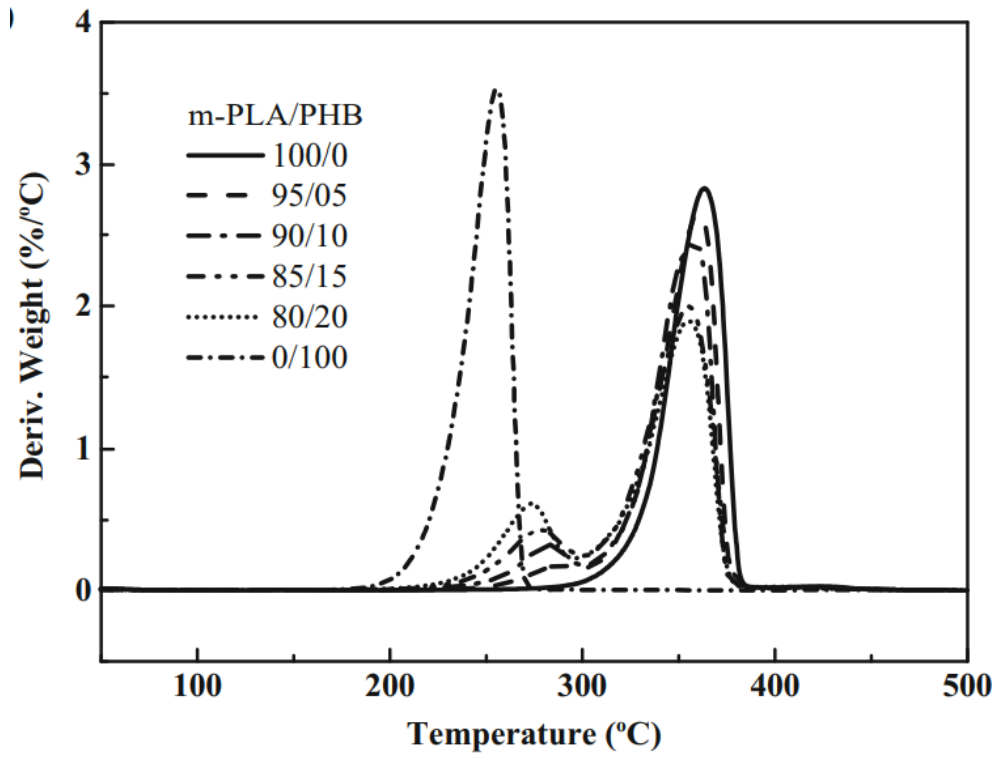


Figure 3: Typical of TGA of PLA/PHB blends by Lai et al. [58] (Copyright 2022, Elsevier).

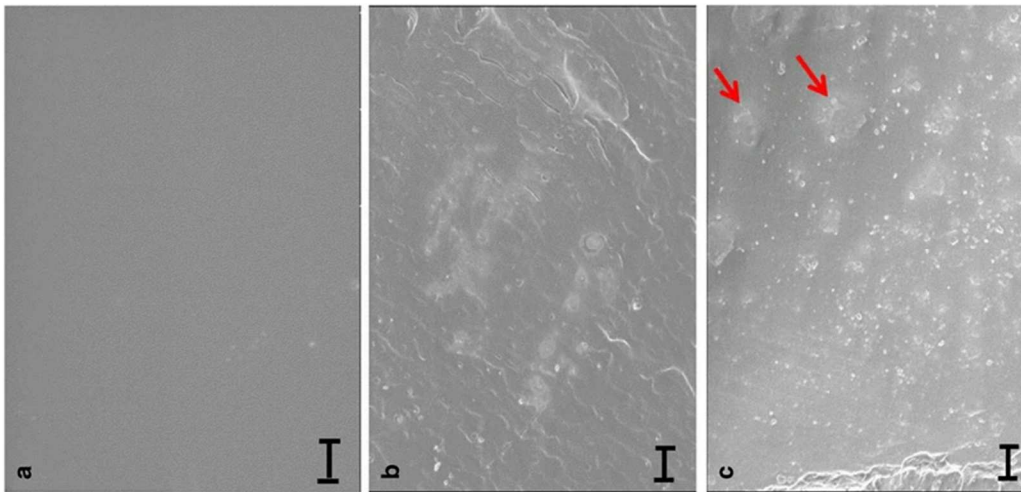


Figure 4: SEM images of fracture surfaces of PLA, PLA90/PHB10 and PLA80/PHB20 samples obtained by Lai et al.[58] (Copyright 2022, Elsevier).

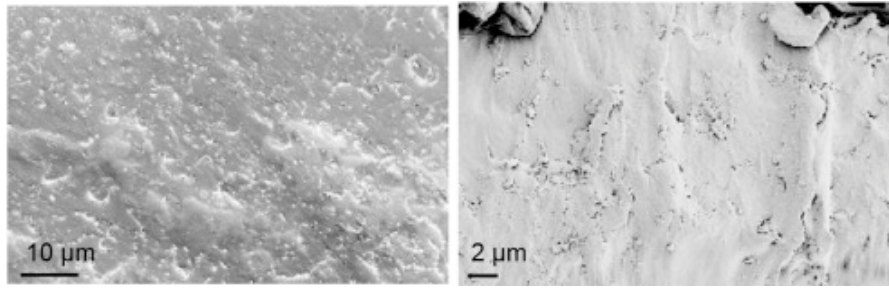


Figure 5: SEM images of fracture surfaces of PLA85/PHB15 blend obtained by Armentano *et al.*[54] (Copyright 2022, Elsevier).

SEM micrographs obtained from cryo-fractured surfaces of these blends are shown in Figure 4. These images are taken from PLA, PLA90/PHB10 and PLA80/PHB20, respectively. White zones are visible in the picture of the ratio 90/10 which corresponded to PHB. In the case of the ratio 80/20, small crystallites of PHB was dispersed in PLA.

The morphology of blends of these polymers depend on the blend composition. When the blend is rich in PLA, PHB is dispersed in PLA with a matrix/disperse- morphology. This morphology was observed for the ratios of 85/15 , 80/20, 75/25 and 70/30 in PLA/PHB blends. By contrast, when PHB is the dominant composition, PLA is dispersed in PHB [37]. Figure 5 shows the SEM images obtained by Armentano *et al.* in which PHB is dispersed in the PLA matrix [54].

Table 2: Thermal stabilities and processing methods of PLA/PHB blends - T_{onset} , T_{max} and residue amount are reported as per composition in PLA/PHB blend.

Ratio	T_{onset} (°C)	T_{max} (°C)	Residue (%)	Processing method - temperatures	Refs.
95/05	287	288 ; 360	NA	Internal mixer – 180 °C	[58] ^a
90/10	273	282 ; 358	NA	Internal mixer – 180 °C	[58] ^a
85/15	NA	349;	NA	Microextrusion – 180 °C, 190 °C, 200 °C	[39]
	NA	280 ; 345	NA	Extrusion – 180 °C, 190 °C, 200 °C	[54]
	261	278 ; 356	NA	Internal mixer – 180 °C	[58] ^a
	NA	349	NA	Microextrusion – 180 °C, 190 °C, 200 °C	[65]
80/20	297.04 ; 363.75	NA	NA	Internal mixer – 160 °C	[55]

	253	274 , 354	NA	Internal mixer – 180 °C	[58] ^a
75/25	270	283 ; 356	0.10	Internal mixer – 175 °C	[38]
	293.81 ; 357.30	NA	NA	Internal mixer – 160 °C	[55]
	NA	102 ; 284 ; 363	0.4	Solvent casting – 55 °C	[29]
	290 ; 335	NA	NA	Microextrusion – 175 °C	[59]
	267	290 ; 359	1.21	Internal mixer – 175 °C and compression molding – 170 °C	[30]
	272	297 ; 366	0.21	Internal mixer – 175 °C and 3D printing – 200 °C	[30]
	266	278 ; 356	NA	Microextrusion – 180,190,200 °C	[36] ^a
	272 (1%)	291 ; 360	NA	Internal mixer – 180 and compression molding – 180 °C	[27]
	277	296 ; 367	0.22	Internal mixer – 175 °C and extrusion – 160,165,165,170,170,170 °C	[30]
	282	286 ; 349	NA		[62]
	208,2	256 ; 334	NA	Electrospinning	[59, 61]
70/30	284.13 ; 300.81 ; 341.70	NA	NA	Internal mixer – 160 °C	[55]
	NA	315 ; 376	2.1	Internal mixer – 180 °C and compression molding – 190 °C	[57] ^c
	NA	270 ; 325	NA	Extrusion – 170-180 °C and compression molding – 180 °C	[53]
50/50	171.2	256 ; 306	NA	Electrospinning	[66] ^a
25/75 25/75	NA	275	2	Miniextrusion – 170,175,180 °C and injection molding – 170 °C	[37]

	215	246 ; 296	NA	Electrospinning	[66] ^a
05/95	NA	274	2	Miniextrusion – 170,175,180 °C and injection molding – 170 °C	[37]

^a : T_{onset} = temperature for 5% mass loss

^b : T_{onset} = temperature for the onset of degradation

^c : TGA at 20 °C/min

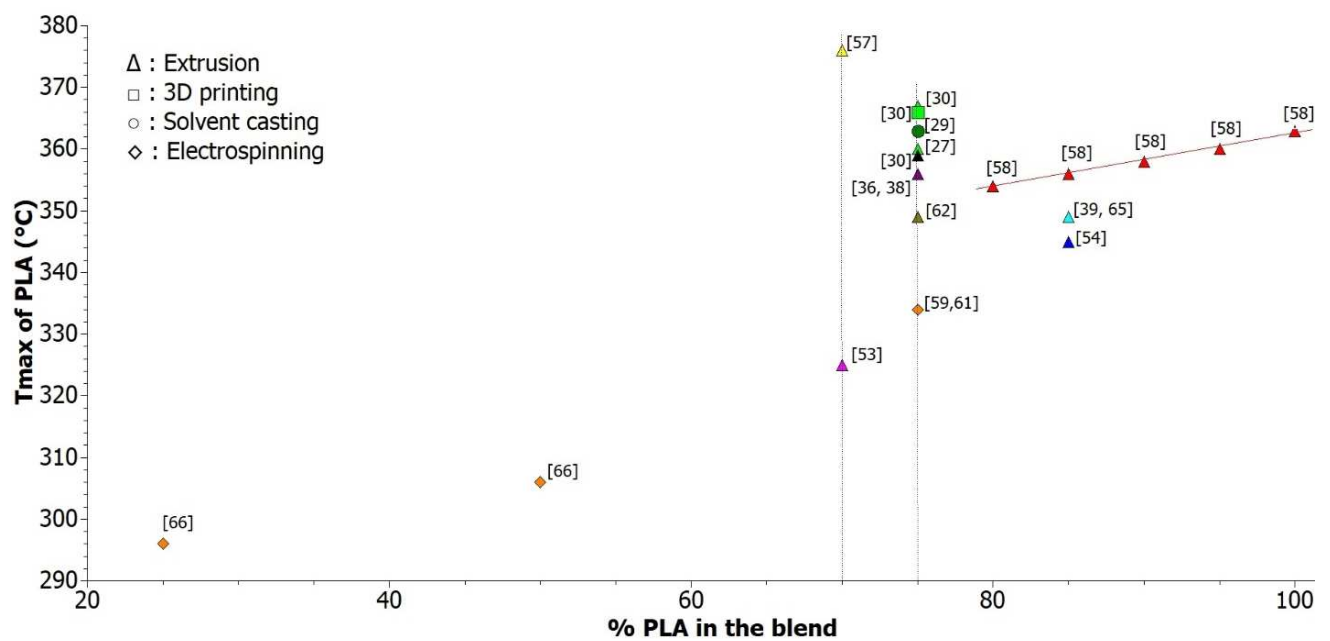


Figure 6: Representation of the values of T_{max} for the PLA/PHB ratios – T_{max} values of PLA in PLA/PHB blend for different processing methods (Δ = extrusion, \diamond = electrospinning, \circ = solvent casting and \square = 3D printing). The percentage of PLA in the blend is in the x axis and the y axis on the left side is the T_{max} value of PLA in the blends.

3. PLA/PHB blends containing additives

The melting temperature of PHB is close to its degradation temperature, which justifies its low thermal stability. As a consequence of such a low thermal stability, PHB has a narrow processing window (between 160 and 190 °C) [67]. In order to expand the use of PHB and PLA/PHB blends, several works examined the incorporation of some additives such as plasticizers [26], [56], cellulose-based reinforcements [36], [37] or crosslinking agents [29], [30]. Generally, plasticizers modify the mechanical properties of the material and make it more flexible, while the reinforcement fillers are targeted to improve the mechanical resistance of the material. Crosslinking agents are used to promote the creation of chemical

bonds between the polymer chains and modify its physicochemical properties. In the case of blends, compatibilizers are used for interfacial adhesion enhancement. Sometimes the aforementioned additives affect the thermal stability of the blend. Herein, the thermal stability of PLA/PHB blends containing different additives are reviewed.

3.1 Thermal stability of PLA/PHB blends containing plasticizers

Plasticizers are generally small molecules with a low used to improve the macromolecular chains motion and thereby the flexibility and processability of materials by lowering their glass transition temperature [68]. Generally, different plasticizers like acetyl tributyl citrate (ATBC), polyethylene glycol (PEG), oligomeric lactic acid (OLA), and vegetal oils are used for the plasticization of PLA/PHB blends.

Arrieta *et al.* [27], used acetyl tributyl citrate to plasticize a 75/25 PLA/PHB blend. Isothermal TGA measurements showed an improvement in the thermal stability of the blend up to 9 min with the addition of 15 wt.% ATBC. However, the dynamic measurements showed no significant change in T_{max} values of PLA and PHB with the addition of ATBC. These results are in agreement with those obtained for the plasticization of PLA and PHB solely with ATBC [28], [60]. In this work, ATBC was compared to PEG which presented the same impact on the PLA/PHB blend. The PEG used is less thermally stable than ATBC but this can be explained by the low molecular weight of the latter (300 g.mol^{-1}). Panaitescu *et. al.* [48] studied the impact of two PEG with different molecular mass on the thermal stability of PHB. PEG4000 has a molecular mass of 4000 g.mol^{-1} and PEG6000 has a molecular mass of 6000 g.mol^{-1} . They observed an improvement in the thermal stability of PHB with the addition of PEG6000 and a decrease in thermal stability with the addition of PEG4000. They concluded that the molecular weight of the plasticizer governs the thermal stability.

Iglesias Montes *et.al.* [56] added glyceryl tributyrate (TB) at 10 wt.%, 15 wt.%, and 20 wt.% into PLA/PHB blends and observed a slight increase of the T_{max} of each polymer compared to the unplasticized blend. T_{max} values increased with the amount of TB : it could be explained by a lubricant effect of the TB which reduced the frictional forces between the polymer chains resulting in a minor degradation. The localization of the plasticizer between the polymer chains restricts the interactions between them and thereby suppresses the thermal degradation.

Vegetable oils have also been used to plasticize PLA/PHB blends. Three different oils are cited in the studies including epoxidized soybean oil (ESBO), epoxidized linseed oil (ELO)

and epoxidized canola oil (ECO). Lopera-Valle *et al.* observed no significant change in the thermal stability of the PLA/PHB blend (75/25) with the addition of 10 wt.% of ECO [59]. The studies by Garcia-Garcia *et al.* and Panaitescu *et al.* [48], [61] showed a strong improvement in the thermal stability of PHB with the addition of ESBO or ELO. Garcia-Garcia *et al.* [61] observed an insignificant increase in the T_{onset} of PHB from 246 °C to 272 °C and 274 °C with the addition of 5 wt.% and 10 wt.% of ELO respectively. In the case of ESBO, the T_{onset} of PHB/10ESBO was less than T_{onset} of PHB containing 5 wt.% ESBO. Based on the TGA analysis of Panaitescu *et al.* [48] the same phenomena was observed. An addition of 5 wt.% of ESBO increased the $T_{10\%}$ of PHB by 3 °C but the addition of 10 wt.% decreased this temperature by 29 °C. According to them, this difference can be explained by incompatibilities between the ESBO and tributyl citrate (TBC), the plasticizer found in the commercially available PHB. This improvement in the thermal stability could be explained by the improved interaction between the vegetal oil molecules and the polymer chains. As a result, the formation of a thin physical barrier on the surface of the material decreases the permeability of volatile products. Moreover, the epoxidized vegetal oils are able to scavenge acids groups during the degradation which improve the thermal stability [61]. This hypothesis suggested a reaction between the carboxylic acid groups resulting from the decomposition of PHB and the epoxy groups to form interchain bonds or crosslinks and shift the degradation to higher temperatures [48].

Oligomeric lactic acid (OLA) has been added in a PLA/PHB blend (85/15) and the addition of 15 wt.% or 20 wt.% of OLA in the blend does not cause a significant change in thermal stability but the addition of 30 wt.% of OLA led to a decrease in T_{max} of 15 °C and an increase in the intensity of the first degradation peak [39]. The same observation was made by Luzi *et al.* [65], the addition of 30 wt.% of OLA decreased the T_{max} of PLA by 13 °C.

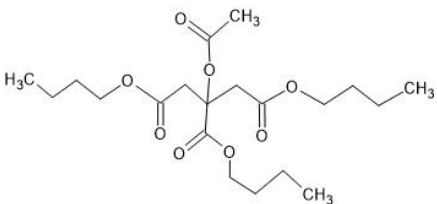
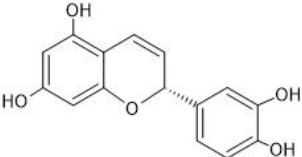
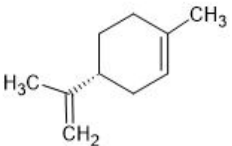
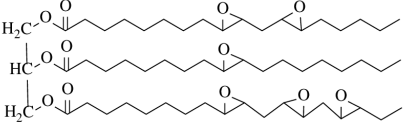
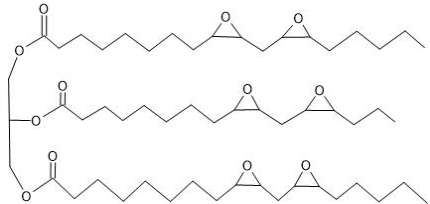
Lapol 108 is a polyester, which has also been used to plasticize a 75/25 w/w PLA/PHB blend. Addition of these plasticizers increased slightly the T_{onset} of the blend. That could be explained by the higher thermal stability of lapol 108. The T_{max} values of PLA and PHB slightly increase by 1 °C with 5 wt.% of lapol 108, but decreased by 15 °C for PLA and stay unchanged for PHB. All the samples had less than 1 wt.% residue at 500 °C but the value increases with the amount of lapol 108 [38].

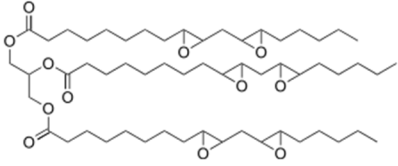
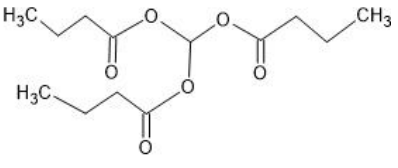
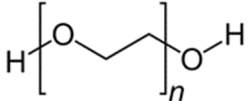
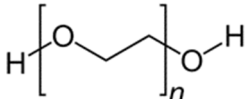
The TGA analysis of a PLA/PHB blend 75/25 containing 15 wt.% of D-limonene showed a first mass loss at 140°C which is attributed to D-limonene as reported by Arrieta *et al.* [26]. It indicated that a part of the D-limonene was degraded before the polymers. Moreover, the

blends with D-limonene showed a lower T_{onset} and T_{max} than the blend without plasticizer. During isothermal analysis the same behavior was noticed, the addition of D-limonene decreased the thermal stability of the blend [26].

Therefore, the major part of the plasticizers tested does not contribute to the thermal stability enhancement of the blends. In some cases, the lubricating effect of plasticizers was adequate to decline the frictional forces between the chains and results on a small improvement of the thermal stability. Sometimes the addition of plasticizers can decrease the thermal stability of the blends and the compatibility between the additives in the commercial polymer and the plasticizer can influence the thermal stability of the blend.

Table 3: Plasticized formulations with names and formula of plasticizers and the ratio PLA/PHB corresponding.

Abbreviation	Name	Formula	wt. %	Ratio PLA/PHB	Refs.
ATBC	Acetyl Tributyl Citrate		15	75/25	[27], [28], [64]
Catechin	-		5	75/25	[28]
D-limonene	-		15	75/25	[26]
eCO	Epoxidized Canola Oil		5 ; 10	75/25	[59]
ELO	Epoxidized Linseed Oil		5 ; 10	0/100	[61]

ESO	Epoxidized Soybean Oil		5 ; 10	0/100	[48], [61]
TB	Glyceril Tributyrate		10 ; 15 ; 20	70/30	[56]
Lapol 108	-	Polyester Mw=80 kDa ; D=26,6	5 ; 7	75/25	[38]
OLA	Oligomeric lactic acid		15 ; 20 ; 30	85/15	[39], [54]
PEG 4000	Polyethylene glycol		5 ; 10	0/100	[48]
PEG 6000	Polyethylene glycol		5 ; 10	0/100	[48]

Arrieta *et al.* observed no obvious phase separation in the presence of the plasticizers, Figure 7 [28]. In the presence of OLA, Armentano *et al.* reported that the surface was modified, as of some micro voids formed on the surface, Figure 8 [54].

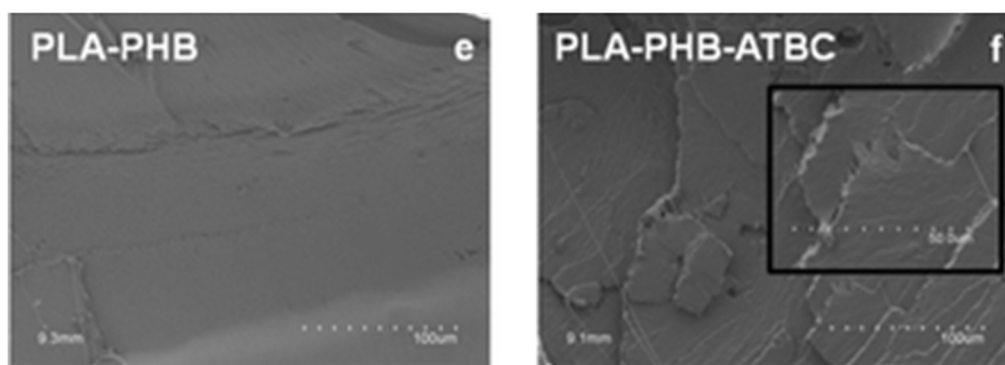


Figure 7: SEM images of fractured surfaces of neat PLA75/PHB25 blend and with ATBC obtained by Arrieta *et al.* [28] (Copyright 2022, Elsevier).

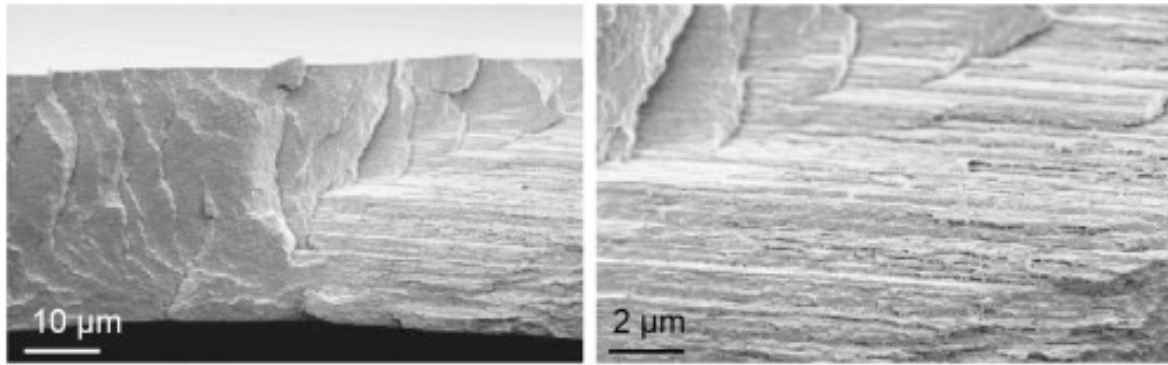


Figure 8: SEM images of fractured surfaces of PLA85/PHB15 plasticized with OLA obtained by Armentano *et al.* [54]
(Copyright 2022, Elsevier)

3.2 Thermal stability of reinforced PLA/PHB blends

The reinforcing additives are used in order to improve the mechanical properties of the polymers. Two families of reinforcement fillers have been used in PLA/PHB blends including cellulose reinforcement (cellulose nanocrystals and nanofibers) [30], [36] and nanoclays (Cloisite 30B and montmorillonite) [53], [57]. Other studies tried to add bio-sourced molecules as catechin [28], [64] or chitosan [64] and observed their effects on the blends. Table 4 introduces different reinforcing agents used to improve the PLA/PHB blends properties.

Aydemir *et al.* [37] showed that adding 1 wt.% or 4 wt.% cellulose nanofibers (CNF) in PLA/PHB blends (5/95 and 25/75) increased $T_{10\%}$, $T_{50\%}$ and $T_{85\%}$ of the blend but the increase of these temperature was more important with 1 wt.%. Arrieta *et al.* [36] reported the effect of cellulose nanocrystals (CNC) and modified cellulose nanocrystals with a surfactant, an acid phosphate ester of ethoxylated nonylphenol (CNCs) on PLA/PHB blend. The incorporation of 5 wt.% of unmodified cellulose nanocrystals (CNC) and modified CNCs in PLA/PHB 75/25 slightly increased T_{onset} from 266 °C to 278 °C. The incorporation of CNC and CNCs increased T_{max1} of 2 °C but decreased T_{max2} of 24 °C and 23 °C respectively [36]. Luzi *et al.* [65] observed a slight decrease of the T_{max} of PLA from 349 °C to 347 °C in the blend with the addition of 1 wt.% of CNC and no variation with 3 wt.% of CNC. Moreover, the addition of CNC in presence of other components as OLA or Carvacrol (antibacterial agent) decreased the T_{max} by 10 °C. The T_{max} of PHB in the blend was shifted to higher temperatures [65]. Frone *et al.* [29] showed a better efficiency of the cellulose nanocrystals to improve the thermal stability thanks to a better dispersion. They also observed a higher final residue rate in the case of cellulose nanocrystals. They suggested a mechanism for the grafting reaction of PLA/PHB with cellulose, Figure 9. The first step is the formation of peroxide radicals thanks

to the presence of dicumyl peroxyde. The peroxide radicals attack polymer chains on carbon atoms with the highest number of hydrogen. Tertial radicals are formed by transformation because they are more stable. In the case of cellulose, the peroxide radicals attack the cellulose on the C6 position of the glucopyranose ring. Then, the radicals of PLA or PHB and cellulose nanocrystals react together and allow to graft PLA/PHB onto cellulose.

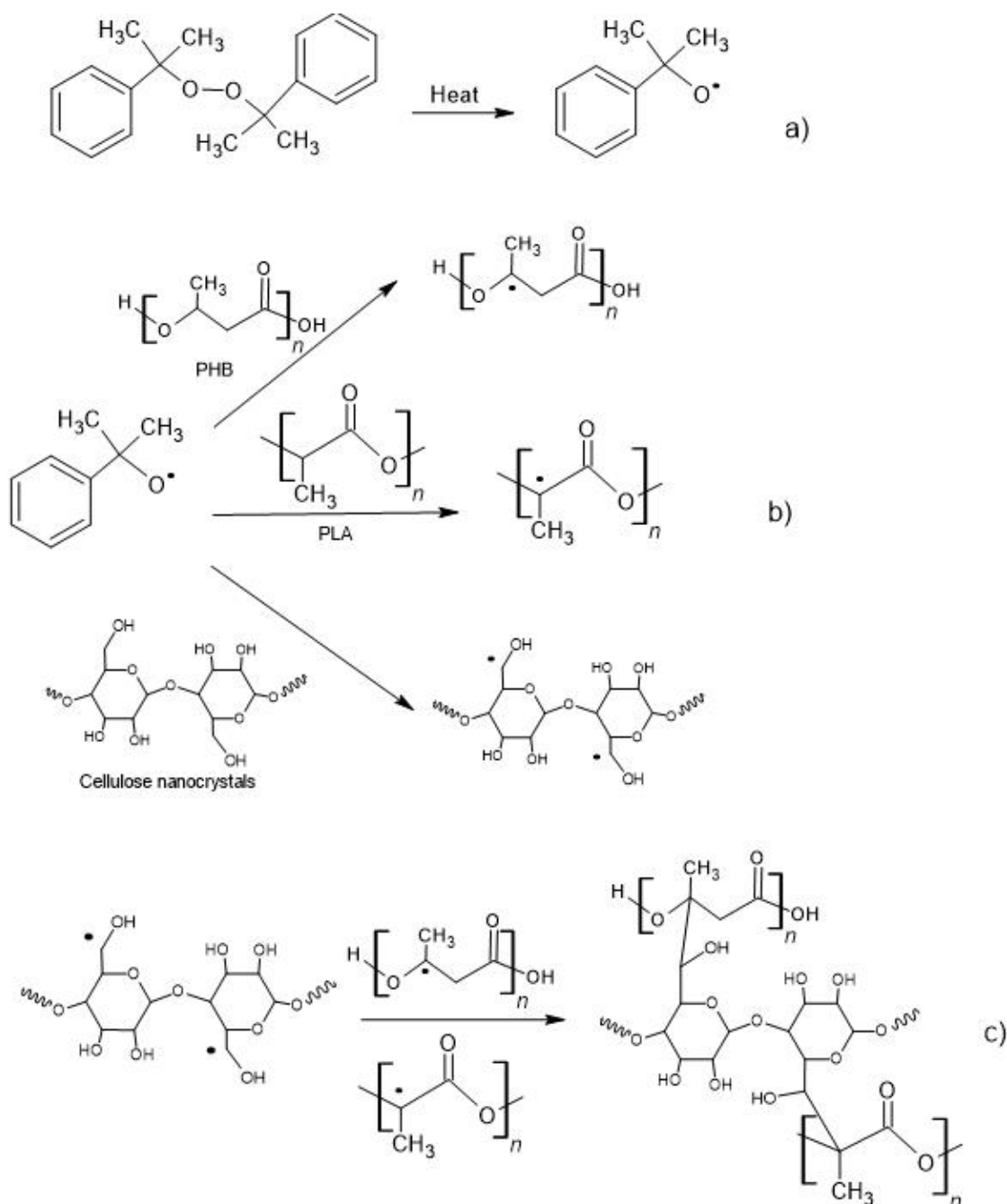


Figure 9: Mechanism of grafting PLA/PHB with cellulose nanocrystals adapted with permission from Frone et al. [30] (Copyright 2022, Elsevier). Under the action of heat the DCP decomposed in peroxide radicals (step a). This radicals react with PLA, PHB or cellulose nanocrystals and are responsible for the formation of radicals of PLA, PHB and cellulose (step

b). The radicals of PLA and PHB react with the cellulose radicals and allow the grafting reaction of PLA/PHB with cellulose (step c).

Frone *et al.* [30] observed a proper dispersion of cellulose nanocrystals (CNC) in the PLA/PHB blend, Figure 10. The images obtained by Aydemir *et al.* (Figure 10) [37] confirms an uniform dispersion of the cellulose nanofibers (CNF) in the PLA/PHB matrix. Although some voids were visible, the interactions between the blend and the nanofibers was strong.

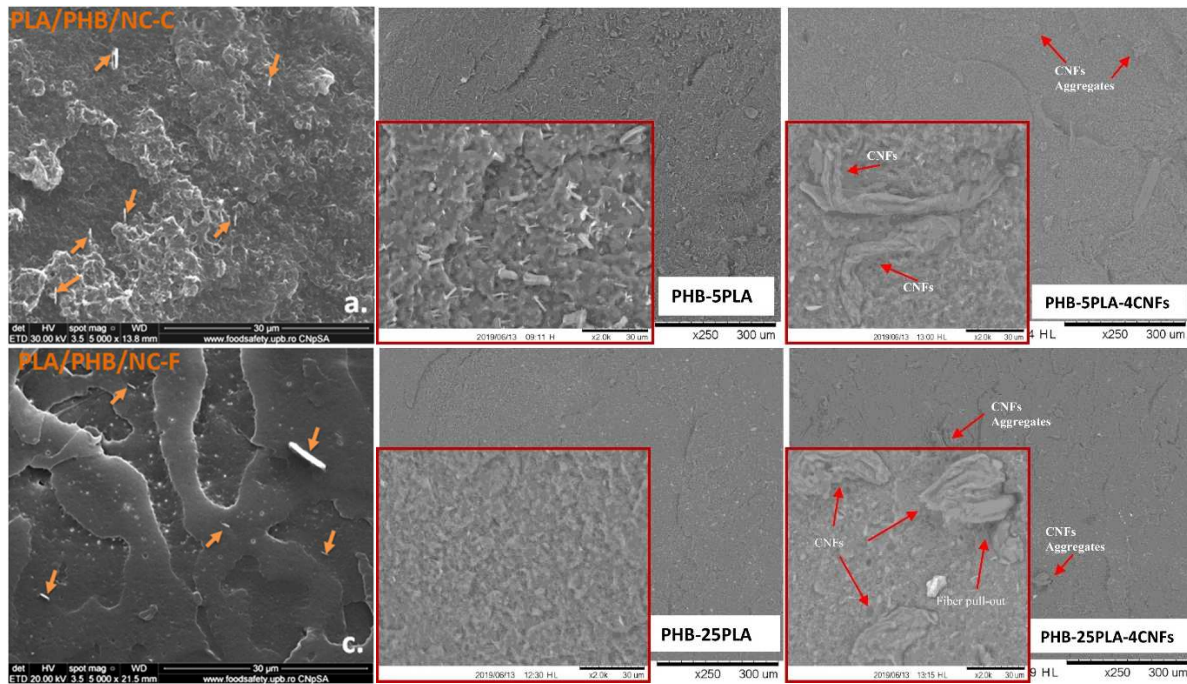


Figure 10: SEM images of fractured surface of PLA/PHB blends reinforced with cellulose nanocrystals (right) and cellulose nanofibers (left) obtained respectively by Frone and al [30]. and Aydemir *et al.* in PLA5/PHB95 and PLA25/PHB75 blends [37](Copyright 2022, Elsevier).

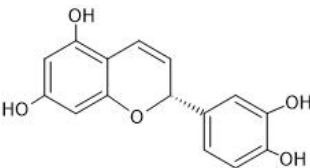
Jandas *et al.* [53] and Pessini *et al.* [57] studied the thermal stability of PLA/PHB blends reinforced with natural montmorillonite (OMMT) and a modified montmorillonite, the Cloisite 30B (C30B). These nanoclays modify the degradation temperature of the polymers blend with an increase of the T_{onset} of PHB, a decrease of the T_{onset} of PLA and an increase of the rate of final residue of the blend. The inorganic fillers improve the char formation during the thermal degradation. The blends with C30B and OMMT showed a residue formation of 4 wt.% after the maximum degradation temperatures even if the OMMT had a better level of intercalation within the blend. This improvement is explained by the decrease in oxygen permeability thanks to the clays [53]. The formation of a long “tortuous path” delays the permeation of oxygen and the escape of volatile degradation products. However, OMMT appears to be more effective than C30B in improving the thermal stability of the blend. The

study by Pessini *et al.* [57] highlights the influence of the location of the nanoclays in PLA or PHB on thermal stability. Indeed, the addition of C30B improved the thermal stability of the blend for any introduction order but the highest values of $T_{10\%}$ and T_{\max} were obtained when the clay is located in a single phase, Table 5. To localize the nanoclays in a single phase, first nanoclays were blended with one polymer over 2 min, then the resulting masterbatch was added to the second polymer. The total mixing time was the same for all the samples.

In presence of ATBC, the addition of 1 wt.% of catechin in PLA/PHB 75/25 blends decreased the $T_{5\%}$ of the blend from 208 °C to 185 °C and increased the T_{\max} of PLA and PHB by 20 °C. The addition of 5 wt.% of catechin showed the same evolution but with a decrease of the PLA T_{\max} by 26 °C [64]. Observations were similar in another study, the addition of 5% of catechin in PLA/PHB blend without ATBC increased the PHB T_{\max} from 275 °C to 279 °C and decreased the PLA T_{\max} from 339 °C to 337 °C [28]. The addition of 1% or 5% of chitosan in presence of ATBC decreased $T_{5\%}$ of the blend from 208°C to 185°C and the PLA T_{\max} but increased the T_{\max} of PHB by 20 °C [64].

The effect of cellulose on the thermal stability of PLA/PHB matrix can vary depending on the cellulose structure. Because of improved dispersion, cellulose nanocrystals are more powerful to improve the thermal stability of the blend. Nanoclays improve the thermal stability of the blend because of the reduction of the oxygen permeability. Moreover when the clays is located in only one phase the thermal stability of the blend seems better with higher values of T_{\max} and $T_{10\%}$. The addition of biobased reinforcement fillers as chitosan or catechin decreased the T_{\max} of PLA in the blend but increased the T_{\max} of PHB.

Table 4: Names, Formulas and amounts of reinforcement fillers and the PLA/PHB ratio corresponding to them.

Abbreviation	Name	Formula	wt. %	Ratio PLA/PHB	Refs.
-	Catechin		1 ; 5	75/25	[28], [64]

-	Chitosan		1 ; 5	75/25	[64]
CNF	Cellulose nanofibers		1 ; 4	95/5 75/25	[29], [37]
CNC	Cellulose nanocrystals		5	75/25	[36], [59]
C30B	Cloisite 30B (montmorillonite modified)		3 ; 5	75/25	[53], [57]
OMMT	Natural montmorillonite		3	75/25	[53]

Table 5: TGA values by Pessini et al. [57] Values of the T₁₀%, T_{max} and the residue rate for the neat polymers, the blend PLA/PHB 70/30 without C30B and the blend with 5wt.% localized in PLA, PHB or interface.

Blend	T ₁₀ % (°C)	T _{max} (°C)	Residue (%)
PLA	302	370	0.9
PHB	275	302	1.2
PLA/PHB	305	315 ; 376	2.1
PLA-C30B/PHB	316	327 ; 381	4.1
PLA/PHB-C30B	312	322 ; 384	4.8
PLA/PHB/C30B	307	317 ; 378	5.0

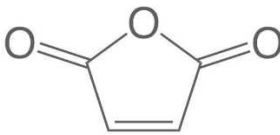
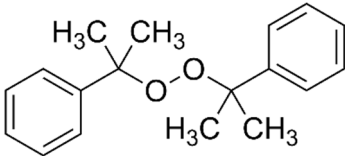
3.3 PLA/PHB blends containing crosslinkers

Some research focused on the crosslinking of PLA and PHB chains [30], [53]. In these studies a crosslinking agent such as maleic anhydride (MA) or dicumyl peroxide (DCP) was added to the blend in order to form bonds between the chains of PLA and those of PHB. The formula of these products is presented in Table 6.

During the reactive extrusion with maleic anhydride, benzoyl peroxide (BPO) was used as an initiator. MA is grafted on the carbon atom of the carbonyl group present on PLA and PHB

chains as illustrated in Figure 6 and Figure 7. According to the authors, the grafting of MA improves the interactions between PLA and PHB chains, and acts as a bridge by the formation of covalent bonds through transesterification reaction, the dipole-dipole interaction or hydrogen bonds, Figure 13, Figure 14. This compatibilization results in a better miscibility of the blend and a modification of the mechanical properties and the morphology of the blend [53]. The addition of MA leads to a slight improvement in the thermal properties of the blend with a no significant decrease of T_{max} of PHB from 270.8 °C to 270.4 °C and a no significant increase of T_{max} of PLA from 325.4 °C to 326.5 °C [53]. Another way to crosslink PLA and PHB is to use DCP. Frone *et al.* [30] added 1 wt.% DCP in a 75/25 PLA/PHB blend and noted no significant change in the T_{max} values. The T_{max} of the blend was 296 °C without DCP and 296 °C with DCP but the T_{onset} and $T_{10\%}$ values decrease respectively of 5°C and 17 °C. MA and DCP was tested on PLA/PHB blends and the first one improved the thermal stability of the blend and more particularly the thermal stability of PHB in the blend while the second one led to a decrease of the $T_{10\%}$ and T_{max} values. The crosslinkers improve the interaction between the two polymers and improve the mechanical properties and the morphology but showed slight changes in the thermal stability. For 70/30 PLA/PHB blend, Jandas *et al.* [53] reported the formation of large voids as a consequence of low miscibility between the two polymers. As already mentioned, the addition of MA as a compatibilizer improved the interfacial adhesion, Figure 15.

Table 6: Formula of maleic anhydride and dicumyl peroxide.

abbreviation	Name	Formula	Refs.
MA	Maleic Anhydride		[53]
DCP	Dicumyl Peroxide		[30]

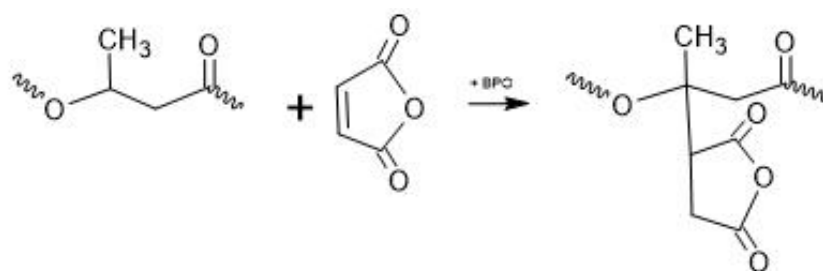


Figure 11: Reaction scheme between of the maleic anhydride on the α -carbon atom of the carbonyl group of PHB adapted with permission from [53](Copyright 2022, Elsevier).

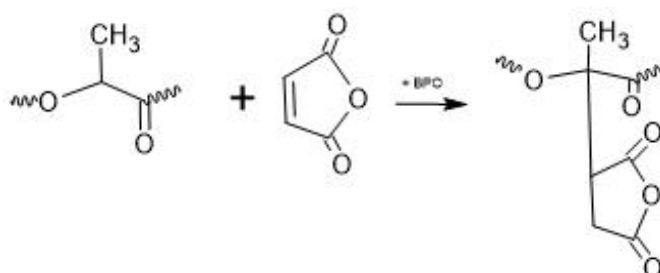


Figure 12: Reaction scheme of the maleic anhydride on the α -carbon atom of the carbonyl group of the PLA adapted with permission from [53](Copyright 2022, Elsevier).

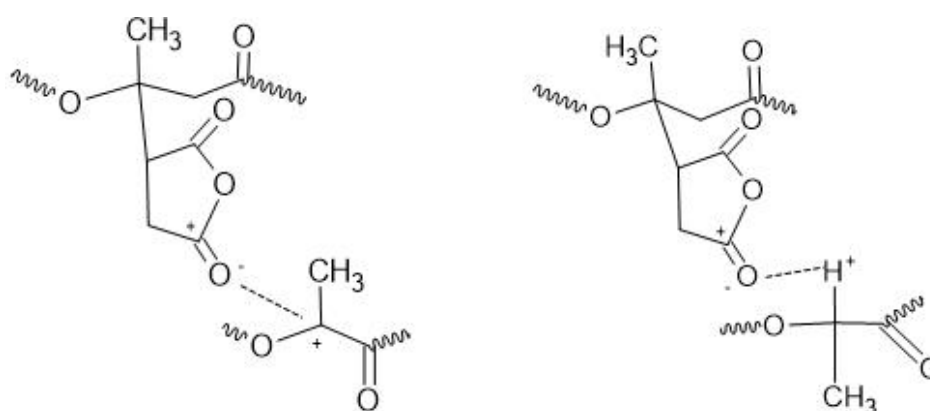


Figure 13: Schematic representation of the interactions between maleic anhydride (MA) and PLA and PHB. MA acts as a bridging unit between the polar unit of PLA and PHB through covalent bond by a transesterification reaction, dipole-dipole and hydrogen intermolecular bond. Adapted with permission from [53] (Copyright 2022, Elsevier).

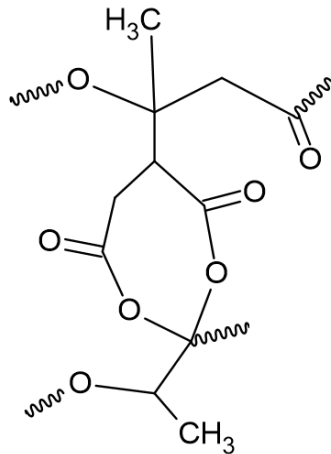


Figure 14: Final product after transesterification between PHB-g-MA and PLA macromolecules adapted with permission from [53] (Copyright 2022, Elsevier).

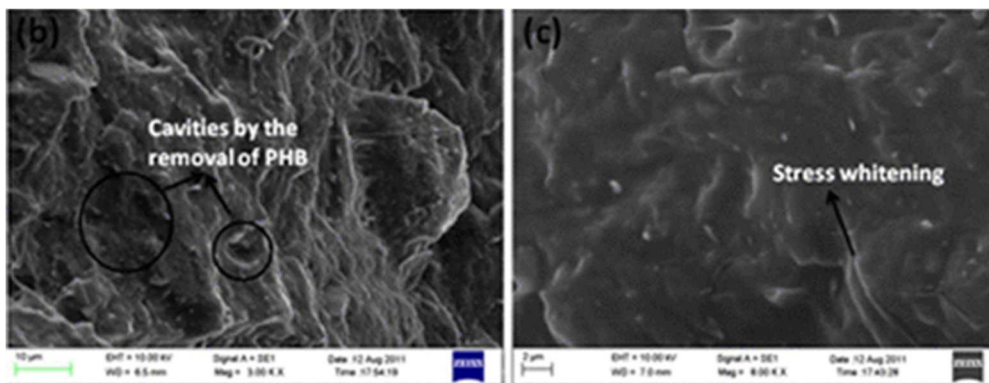


Figure 15: SEM images fractured surfaces of neat PLA70/PHB30 blend and PLA70/PHB30/MA7 obtained by Jandas *et al.* [53] (Copyright 2022, Elsevier).

4. Effect of the processing on the thermal stability of PLA/PHB blends

Frone *et al.* [30] compared the thermal stability of samples prepared with three different method: compression molding, extrusion and 3D printing. The formulations studied were a neat PLA/PHB blend, a blend of PLA/PHB with DCP (PLA/PHB/DCP), a PLA/PHB blend with nanocrystals of cellulose (PLA/PHB/CNC) and a blend of PLA/PHB with DCP and cellulose (PLA/PHB/DCP/CN). To prepare these blends, the PLA and PHB pellets were dried at 80 °C for 4h and introduced into a Brabender Plasticorder LabStation at 175 °C, 60 rpm and 8 minutes. The cellulose and DCP have been added when the polymers were melted. After this step, one part of the blend was molded by compression molding at 170 °C and 10 MPa during 60 seconds and the second part was extruded as a filament for 3D printing. The temperatures of six heating zones of the extruder were fixed at 160 °C, 165 °C, 165 °C, 170 °C, 170 °C, 170 °C, respectively from the hopper to the die. The filament was used to print

samples molten at 200 °C and a plate temperature of 60 °C. ~~The processing temperature was~~ The filament was used to produce the printing samples. The TGA analysis of the PLA/PHB blend showed a maximum value of T_{onset} for the sample prepared by extrusion. When the blend was prepared by extrusion the T_{onset} is 5 °C higher than the T_{onset} of the blend prepared by 3D printing and 10 °C higher than the blend prepared by compression molding. All the characteristics temperature of TGA analysis of the blends prepared by compression molding were lower than those prepared by the other methods. The $T_{10\%}$ was 24 °C lower than blends by extrusion and 3D printing and the T_{max} values were 7-8 °C lower. However, the mass loss at 200 °C and the residue were higher for the blend by compression molding. The study of the PLA/PHB/DCP blends showed a difference between the 3D printing and the other methods. The degradation began at 255 °C for the 3D printing method and at 268 °C and 272 °C for the compression and the extrusion. For this blends the higher values of mass loss at 200 °C and of residue were also for the method of compression molding. This difference can be explained by the effect of DCP on the formation of low molecular weight compounds during the printing and the formation of free radicals. The behavior of the blend with cellulose nanocrystals according to the processing method was similar to the blend PLA/PHB. The addition of cellulose nanocrystals in the blends with DCP stabilized the blend and reduced the difference between the three methods. The T_{onset} of the blends prepared by extrusion, compression molding and 3D printing are respectively 276 °C, 270 °C and 267 °C. This improvement of the thermal stability can be explained by the formation of an improved interface between PLA and PHB thanks a better interfacial adhesion in presence of DCP [30]. Moreover, the nanocrystals of cellulose contain sulphate moieties which can be inactivated during the cross-linking reaction with DCP and delay the degradation. Thus, for all the blends the method which has made it possible to have the better thermal stability is the extrusion. They suggested that this better thermal stability can be due to the induced macromolecular chains orientation during the process. The compression molding method has the lower thermal stability, and it can be caused by a crystallization of PLA induced by the hot stretching and tensile forces.

5. Degradation mechanism

5.1 Decomposition mechanism of PLA

Kopinke *et al.* [35] and McNeill *et al.* [69] observed mainly the formation of several products including lactides, cyclic oligomers, acetaldehydes, carbon monoxides, carbon dioxide, and acrylic acids. Acrylic acid is produced during the cis-elimination reaction and the other products result from the trans-esterification reaction with the formation of monomers, dimers or oligomers, Figure 16. Quantitative analysis showed that the cis-elimination reaction contributed to less than 5% of the overall degradation mechanism. It demonstrated that the majority reactions are the inter- and intra- molecular transesterification reactions via non-radical and radical way. The non-radical way is an attack of the -OH function located at the end of the chain, either hydroxyl or carbonyl on the -CH-O- bond. The radical way is a homolysis reaction of the macromolecular chain that happened on -CH-CO- and -CO-O- bonds with formation of terminations reactive alkyloxy or acyloxy units under the effect of high temperature. The degradation conditions have an influence on the degradation of the PLA and particularly on the products formed. McNeill *et al.* [69] carried out their thermal volatilization analysis under an inert atmosphere but in an enclosed environment. The degradation of PLA was in a sealed glass tube and after cooling, the volatiles were studied by Thermal Volumetric Analysis. They observed a phenomenon of recombination of the dimers and oligomers formed which, even vaporized which remained present in the atmosphere and could therefore react. These reactions are known as esterification equilibrium. Kopinke *et al.* [35] worked under an inert atmosphere but in an open environment allowing the evaporation of volatiles. The decomposition products were analyzed but didn't stay in the reactional environment and didn't react with the other products. They concluded that the possibility of recombination is linked to the evaporation of the various dimers and oligomers, and therefore to their boiling point or sublimation point in the case of dilactides.

Thermal degradation can also be promoted due to the presence of active groups at the end of chains, catalytic residues, monomers, dimers or oligomers, and any other impurities (plasticizers, nucleating agents, fillers) [70].

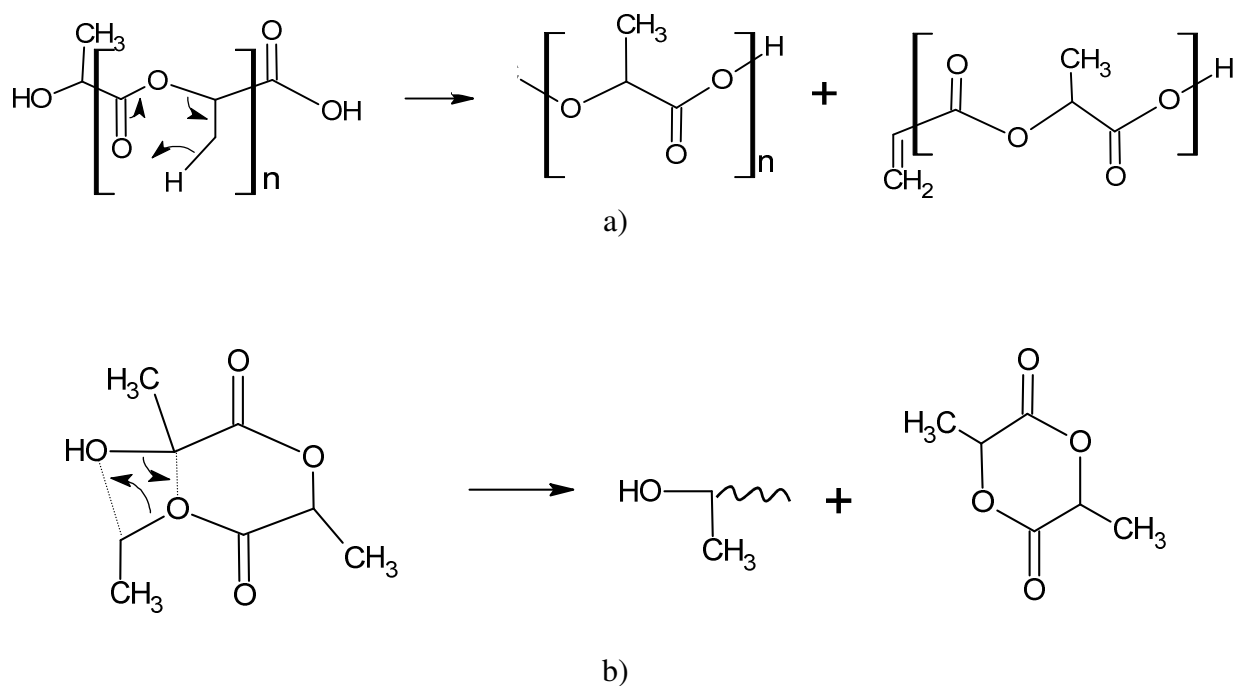


Figure 16: Thermal degradation of PLA by cis-elimination (a) transesterification (b). During the thermal degradation of PLA two reactions can be observed: a random scission of the chains or a transesterification reaction responsible of the formation of cyclic oligomers. Adapted with permission from [35] (Copyright 2022, Elsevier).

5.2 Decomposition mechanism of PHB

In general, the thermal decomposition mechanism of PHB is almost exclusively a random chain scission by cis-elimination leading to a decrease in the molecular weight of the PHB chains (Figure 10) [40]. It takes place between 170°C and 200°C [72]. Several studies confirmed that the main reaction during thermal degradation of PHB are cis-elimination [40], [73], [74], a non-radical random chain cleavage (Figure 11).

Some works suggested other minor reactions taking place during the thermal degradation of PHB [35], [75], [76]. Lehrle *et al.* [77], [78] observed a difference with the theoretical predictions of the statistics of random scission and suggested that this difference could be explain by reactions induced by the end groups. Kim *et al.* [76] also suggested an influence of the end-groups on the thermal degradation of PHB. Kopinke *et al.* [35] noted that the isothermal ATG curve at 270 ° C did not agree with theoretical models of random reactions. They also observed a high activation energy of 380 kJ/mol and they proposed an auto-catalytic reaction to explain this. Galego and Rozsa [79] came the same conclusion and suggested that crotonic acid produced during the reaction act as a catalyst to explain high values of activation energy. Nguyen *et al.* [80] also suggested the occurrence of auto-

acceleration in the PHB thermal degradation at 190 °C based on the changes in molecular weight. This hypothesis is based on the differences between the theoretical and experimental β -degradation activation energies and on the difference of the activation energies between each study. The activation energies determined during the pyrolysis of PHB situate in a very wide range of energies between 110 and 380 kJ.mol⁻¹ [75]. In order to avoid the influence of some complex parameters such as the method used, the presence of residual metal ions or multiple secondary reactions, the value of the activation energy was calculated from the change in molecular weight over a temperature range from 170 °C to 200°C by Nishida *et al.* [81]. This hypothesis was confirmed by the analysis of the results of Nguyen *et al.* by Ariffin *et al.* [75], [81]. The degradation of PHB begins with a non-catalytic random degradation and will progressively evolve into an autocatalytic random reaction [75]. They also showed that the end groups can speed up the reaction. The crotonyl group has a significant accelerating effect for the β -elimination on the neighboring ester group. Thus, this acceleration effect induces the generation of a crotonic acid and a new crotonyl chain end, repeating the same reaction as the unzipping reaction, Figure 11.

This fact was confirmed by Herrera and Kao [82], who studied the thermal degradation of PHB by TGA coupled with Fourier-transform infrared spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR). They confirmed the presence of crotonic acid, as demonstrated by the presence of bands at 3064 cm⁻¹, 1662 cm⁻¹ and 1148 cm⁻¹, respectively corresponding to the bonds = C-H, C = C and C-O. The presence of a band at 1756 cm⁻¹ suggests the presence of ester groups in the products released. The analysis of the PHB degraded at 303°C confirms the release of ester during degradation. The investigation by NMR highlights the presence of non-volatile oligomers in the degraded sample. In addition, despite a two-step degradation, the presence of carboxylic acid and ester was detected only in the first step. It suggested that a random chain scission reaction might take place during degradation of PHB.

In some cases, when PHB contains the carboxylate salts in the end groups, it assists degradation at low temperatures (120 °C) via an intermolecular α -deprotonation reaction by carboxylate [51].

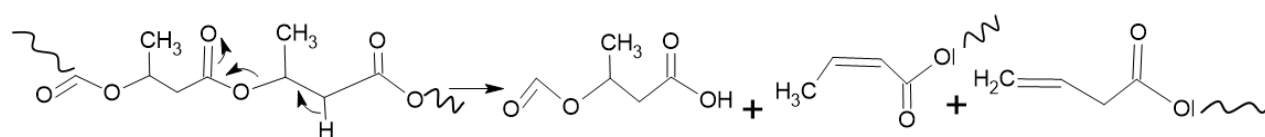


Figure 17: Thermal degradation of PHB by cis-elimination. The main decomposition reaction of the PHB is a random chain scission by cis-elimination. This reaction is responsible for a decrease of the molecular weight and the formation of crotonic acid. Adapted with permission from [83] (Copyright 2022, Elsevier).

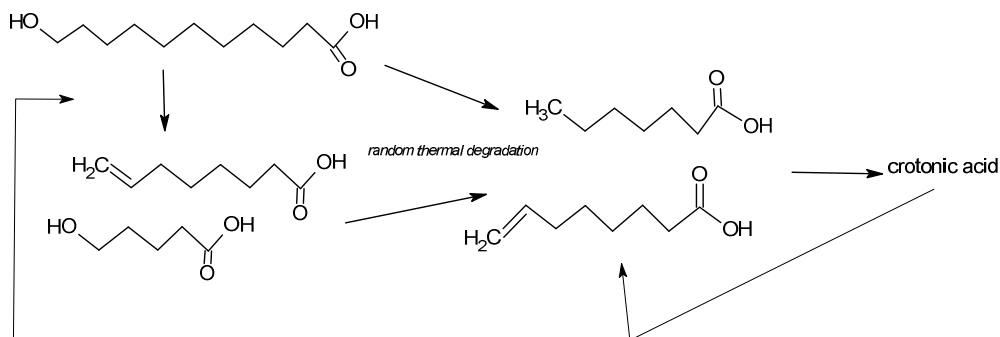


Figure 18: Auto-acceleration and degradation phenomena of PHB. The crotonic acid formed during the reaction can catalyze the random chain scission reaction. The reaction is auto-accelerated by the presence of crotonic acid. Adapted with permission from [75] (Copyright 2022, Elsevier).

6. Summary and future perspectives

PLA is the most frequently used renewable polymer, but to improve its properties such as crystallinity index, barrier properties and biodegradability it should be blended with PHB, another biosourced polymer from green polyester family. The thermal properties of the neat PLA and the neat PHB are compared with the thermal properties of PLA and PHB in PLA/PHB blend with and without plasticizers, reinforcement fillers or crosslinkers.

In the PLA/PHB blends, the thermal stability of PHB is improved by the addition of PLA, while the thermal stability of PLA is slightly decreased in the blends. For example, in the study of Lai *et al.* [58], the T_{\max} of PLA shifted from 363 °C for the neat PLA to 354 °C in a 80/20 w/w PLA/PHB, blend whereas the T_{\max} of PHB increased from 255 °C to 274 °C.

The choice of the plasticizers is important because all the plasticizers have not the same influence on the thermal properties of the blend. The major part of the reinforcement fillers showed the same trend with respectively an increase and a decrease of the decomposition temperatures of PHB and PLA. Cellulose has a higher efficiency in the form of nanocrystals, due to a better dispersion in the blend. Moreover, the addition of clays improved the formation of char, and it was suggested that the thermal properties of the blend can change with the localization of the clays in the different phases of the blend. The use of crosslinkers improved the mechanical properties and the miscibility between PLA and PHB but didn't

show significant changes in the thermal properties. The method of processing the blend can influence the thermal stability of the PLA/PHB blends.

The main steps of the decomposition mechanism of PLA and PHB are known, but some doubts exist about the reactions affecting the degradation of these polymers. TGA coupled with FTIR and pyrolysis gas chromatography coupled with mass spectrometry (Py-GC/MS) might be solutions to identify precisely the decomposition mechanisms of PLA and PHB. We need such combinatorial analyses in order to sketch a full picture of the phenomenon taking place in the course of thermal decomposition of these polymers and their reaction products.

A synergistic effect between PLA and PHB at ratios of 75/25 and 70/30 was mentioned in several studies, but not generally verified. Modification of the thermal properties of the PLA/PHB blend is a good way to give reason for industrial application of these biopolymers. Currently, PLA is the subject of much research works to improve its fire properties, but studies on the fire properties of PHB and on PLA/PHB blend are in early stages. Developing these subjects could make it possible to determine if these two polymers and their blends can be credible alternatives to the usual polymers.

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