

Heat Resistance of Biobased Materials, Evaluation and Effect of Processing Techniques and Additives

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The paper describes the effect of different manipulations (addition of fiber, nanoclay, nucleating agents and chain extender, blending, annealing, use of a higher mold temperature and stereocomplexation) on the heat resistance of poly(lactic acid) (PLA) and poly(hydroxybutyrate) (PHB). Therefore, the differential scanning calorimetry profiles, the vicat softening temperatures and the degradation temperatures were measured and compared to standard PLA, PHB, and polypropylene (PP) as reference materials. Furthermore, a comparison between VST and HDT as parameters for heat resistance was made by examining the deformation during contact with hot water. Stereocomplexation and the use of a higher mold temperature seemed the best techniques to obtain PLA-based materials with good heat resistance, while other manipulations had little to no effect on the processed biopolymer. The addition of chain extender to PLA and PHB had no effect on processed polymers, but it did improve the thermal degradation of PLA during processing. Furthermore, hot fill tests showed that higher VST values were more reliable as a heat resistant parameter than HDT values for these kinds of application. The VST values of PHB were similar to PP, suggesting that PHB also provides opportunities as a packaging material for food products that undergo a heat treatment. POLYM. ENG. SCI., 00:000–000, 2017. © 2017 Society of Plastics Engineers

INTRODUCTION

Currently most packaging materials used in the food industry, such as polyethylene terephthalate (PET), polyethylene (PE), polypropylene (PP), and polystyrene (PS), are fossil fuel based. These materials are intensively used because of their good functionalities, low cost and high availability. But, their petrochemical nature means they depend on the rising and fluctuating oil prices, and raises concerns regarding their environmental impact. Materials made from renewable resources could be a sustainable alternative. Biobased food packaging uses biomass which regenerates (annually), saving fossil resources, and they have the potential of being carbon neutral [1–3]. However, the heat resistance of most of these biobased plastics is insufficient for use as a packaging material for foods undergoing a heat

treatment before or after packaging. This means that these materials cannot be used for in-package sterilization or pasteurization, hot fill packaging or microwave and oven applications, which are important features in nowadays packaging concepts. Furthermore, a poor heat resistance can also lead to degradation of the polymer during processing.

Increasing the heat resistance of biopolymers (both during and after processing) can be achieved in several ways. A *first technique* is the use of additives such as plasticizers, chain extenders, nanoparticles, or nucleating agents. The addition of plasticizers can increase the polymer chain mobility which can enhance the crystallization rate by reducing the energy required during crystallization [4]. Wang et al. [5] found that the addition of N-octyl lactate (NOL) lowered the glass transition temperature (T_g) with maximum 17.8°C, depending on the NOL content. Furthermore, the crystallization temperature (T_c) and melt temperature (T_m) also decreased with increasing plasticizer content. The percentage crystallinity increased with increasing NOL content. Boonfaung et al. [6] found that the addition of polypropylene glycol, polyethylene glycol-ran-propylene glycol, dioctyl phthalate, tributyl citrate, and adipic acid lowered the T_g by maximum 15.4°C. Furthermore, these plasticizers also decreased the T_m of PLA, allowing processing of the polymer well below the degradation temperature. Martin and Avérous [7] reported similar results after the addition of polyethylene glycol to PLA. They also found an increase in the degree of crystallinity, which is a parameter closely related to heat resistance. The addition of a chain extender can prevent the thermal degradation of polymers during processing by extending the polymer chain and increasing the molecular weight (by re-coupling of degraded chains) and by decreasing the number of reactive polymer ends, resulting in a lower chance of back-biting [8, 9]. Al-Itry et al. [10] found that the viscosity of PLA and PLA/polybutyrate adipate terephthalate (PBAT) remained constant in time after addition of Joncryl[®]. This indicates a reduced thermal degradation during processing. Also TGA analysis showed that the degradation temperature increased by 20% (1% Joncryl[®] m/m). But for poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), a lower crystallization temperature and crystallinity was found after addition of Joncryl[®] [11]. The positive effect of the addition of nanoparticles was demonstrated by Ray [12, 13], who found that the addition of montmorillonite (MMT) clay and organically modified synthetic fluorine mica to PLA increased the heat

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deflection temperature (HDT) with 17°C and 39°C, respectively. Furthermore, addition of nanoclay or nanocellulose to PLA or PLA/PHB improved the degradation temperature according to Martino et al. [14] and Arrieta et al. [15]. However, other studies show that the addition of nanoparticles to PLA resulted in a lower degradation temperature [9, 16–18].

A *second technique* to increase the heat resistance is the use of blends and copolymers. Blending of PLA with PHB decreased T_g and the post-crystallization temperature (T_c) compared to pure PLA and increased the degree of crystallinity by 5% [15]. A more constant viscosity, better elongation and strength can be achieved by blending PLA with PBAT [19, 20]. Copolymers of PHB and polyhydroxyvalerate (PHV), resulting in poly(3-hydroxybutyrate-3-hydroxyvalerate) (PHBV), have a decreased T_m and T_g compared to pure PHB [21]. The T_m , T_g and crystallization of stereoblock and stereo-complex PLA (PLLA and PDLA) are much better than the ones of pure PLA. The HDT of amorphous PLA and stereo-complex PLA is 55°C–60°C and 160°C–200°C [22, 23], respectively.

The incorporation of a filler, making a biocomposite, is a *third technique* to increase the heat resistance. The HDT of a PHBV/woodfiber composite and PHBV/bamboofiber composite increased with 24°C and 9°C (40 wt% of fiber), respectively [24, 25]. Finally, a *fourth technique* is the adjustment of the processing parameters to increase the heat resistance. Harris and Lee [26] found that the degree of crystallization and the HDT increased with increasing annealing time.

Although the interest in biobased plastics is growing, a lot of stakeholders in the food industry are doubtful regarding the introduction of biobased plastics. This can be attributed to different factors including amongst others higher prices and the lack of knowledge regarding these new materials and their possibilities. Therefore, in this study, several commercially available materials with one of the previous described techniques were tested and the effect on the heat resistance was measured. Although these techniques were described in literature before, comparability of the results is very difficult, since different standards or testing conditions were used. The evaluation of this quantity of techniques on the heat resistance of biobased polymers by these quantities of different measurements, allowing for a uniform comparison has not yet been described in literature. The results of this research are immediately applicable in industry. Furthermore, a comparison between HDT and VST as an indicator for the thermal properties was made, since mostly only one of these parameters is measured/given.

EXPERIMENTAL

Materials

The tested polymer materials (commercially available) and additives were supplied by different producers (Table 1) and processed at the Centre for Polymer and Material Technologies (CPMT, Ghent University, Ghent, Belgium) based on the technical specifications provided by the producers. As reference materials, two standard biobased polymers (PLA and PHB) and a

TABLE 1. Overview tested materials, their use and their suppliers.

Material	Use	Producer/supplier
	Standard materials	
NatureWorks Ingeo® 3052D (PLA)	Injection	NatureWorks LLC ^a
NatureWorks Ingeo® 6400D (PLA)	Extrusion	NatureWorks LLC
Sabic PP 575P (PP)	Injection	Sabic Europe ^b
Total PPC 5752 (PP)	Injection	Total ^c
Biomer® P304 (PHB)	Injection	Biomer ^d
	Modified materials	
Sogreen™ 2001-A (PLA/PHB)	Extrusion	GreenGran ^e
GreenGran PO21J (PLA + 25% fiber)	Extrusion/Injection	GreenGran
Synterra® IM (stereocomplex PLA (sc-PLA))	Injection	Synbra/Purac ^f
1A-115/13A0 (PLA compound)	Injection	Company A ^g
1A-131/14CC (PLA compound)	Injection	Company A
	Additives	
Joncryl® FA1009 masterbatch ^h	Chain extender for PLA	BASF ^j
Joncryl® FA11005 masterbatch ⁱ	Chain extender for PLA	BASF
Cloisite 15A (montmorillonite)	Polymers	Rockwood additives/BYK-Gardner ^k
Hyperform HPN-20E®	Nucleating agent	Milliken ^l
Hyperform HPN-68L®	Nucleating agent	Milliken

^aBlair, NE.

^bSittard, The Netherlands.

^cCourbevoie, Île-de-France, France.

^dKrailling, Germany.

^eEde, The Netherlands.

^fEtten-Leur, The Netherlands.

^gConfidential.

^h25% (w/w) Joncryl® ADR 4368 in PLA carrier.

ⁱ25% (w/w) Joncryl® ADR 4300 in PLA carrier.

^jArnhem, The Netherlands.

^kGeretsried, Germany.

^lGhent, Belgium.

TABLE 2. Processing parameters for injection molding of different biobased and reference materials.

Material	Temperature profile (°C)						Screw speed (rpm)	Injection 1		Injection 2		Pressure		Cooling time (s)
	Mold	Nozzle	Screw (zones U.A.B.C)			Speed (mm/s)		Pressure (bar)	Speed (mm/s)	Pressure (bar)	Pressure (bar)	Time (s)		
Sabic PP 575P	15–40	230	230	220	210	190	288	57	580	40	507.5	507.5	3	25
Ingeo™ 3052D	25	210	210	200	190	180	288	57	580	17.1	290	217.5	3	20
GreenGran PO21J	30–70	160	140	150	160	170	200 ^a	57	580	17.1	290	217.5	3	20
Ingeo™ 3052D + 2% Joncryl® FA 1009	25	210	210	200	190	180	288	57	580	40	507.5	507.5	4	20
Ingeo™ 3052D + 2% Joncryl® FA 11005	25	210	210	200	190	180	288	57	580	34.2	435	362.5	4	20
Biomer® P304	40	170	170	175	175	185	288	91.2	1160	11.4	145	362	4	20
Biomer® P304 + 2% Joncryl® FA 1009	40	170	170	175	175	185	288	91.2	1160	11.4	145	362	4	20
Biomer® P304 + 0.1% Hyperform® HPN 20E or HPN 68L	35	170	170	175	175	185	288	91.2	1160	11.4	145	362	4	20
PLA blend	35	205	205	195	185	175	288	57	725	29	368	362	5	25
Synterra® IM	90–100	195	160	190	200	195	175	57	580	17.1	290	217.5	3	35
PLA compounds	30–100	155	165	175	190	160								30–60–90

heat resistant conventional polymer (PP) were chosen. By means of both injection molding and extrusion, beakers (Engel 80T injection molding machine, Schwertberg, Austria) and/or tensile bars (Boy 22S injection molding machine, Neustadt-Ferndthal, Germany) or extrusion plates (Brabender® single screw extruder, Duisburg, Germany) were made. The processing parameters are shown in Table 2 (injection-molding) and Table 3 (extrusion).

Differential Scanning Calorimetry

The percentage crystallinity α_c , the glass transition temperature (T_g), the melt temperature (T_m), and the crystallization temperature during heating (cold crystallization temperature, T_{cc}) or during cooling (crystallization temperature, T_c) of the processed materials were determined by differential scanning calorimetry (DSC) (DSC 204 F1 Phoenix®, Netzsch, Selb, Germany, yearly calibrated by metal standards). 15–30 mg of sample was heated in an aluminum pan from room temperature (20°C) up to max. 250°C and cooled down at a constant rate of 10°C/min under a N₂ atmosphere (20 cm³/min). Since the material characteristics are important, two runs were performed for each material. The second run is performed to erase the previous thermal history and to understand the ability of the polymer to recrystallize after melting. Results were processed via Proteus® thermal analysis program (v.4.8.5, Netzsch-Geraetebau GmbH). The theoretical melting enthalpies used for a 100% crystalline material ΔH_m^c

were 135 J/g for PLA [27], 209 J/g for PP [28], and 146 J/g for PHB [29]. All DSC results reported are single measurements.

Vicat Softening Temperature (VST)

To determine the VST, bars with a thickness between 3 and 6.5 mm were heated in an oil bath at a constant rate of 50°C/h or 120°C/h. A needle with a surface area of 1 mm² and with a downward force of 6.1 N or 12.2 N was set to penetrate the bar until the needle effectively penetrated the bar by 1 mm (CEAST 6510-517, Turin, Italy). Samples were tested in duplicate.

Heat Deflection Temperature (HDT)

To determine the HDT, samples were heated in an oil bath at a constant rate of 120°C/h after conditioning for 5 min (CEAST 6510-517). A force of 0.49N was used to bend the samples. According to ISO-75B edgewise, the HDT was reached for a 0.34 mm deflection of the sample. Samples were tested in duplicate.

Thermogravimetric Analysis (TGA)

TGA tests were performed with a Netzsch STA 449 F3 Jupiter (Netzsch-Geraetebau GmbH, Selb, Germany). 15–25 mg of sample was heated at a constant rate of 10°C/min from room temperature (20°C) till maximum 750°C (dependent on the material) under nitrogen atmosphere. Results were processed with the Proteus® Thermal analysis program (v.5.0.1, Netzsch-Geraetebau). The

TABLE 3. Processing parameters for extrusion of different biobased materials.

Material	Temperature profile screw (°C)					Screw speed (mm/s)	Top roll (°C)	Middle roll (°C)	Bottom roll (°C)
GreenGran PO21J	35	160	170	170	170	200	25	38	50
Sogreen™ 2001-A	35	160	170	170	165	200	25	38	50
Ingeo™ 6400D	35	160	170	180	190	300	25	38	50
Ingeo™ 6400D + 5% (w/w) Cloisite 15A	35	160	170	180	190	300	25	38	50

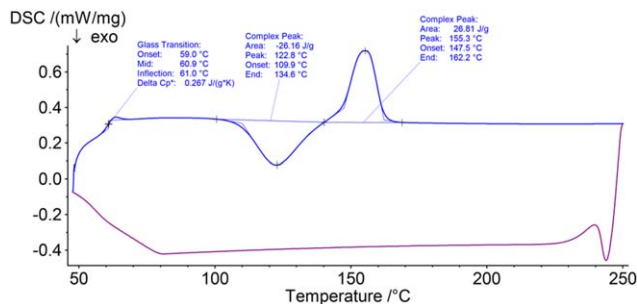


FIG. 1. DSC profile of NatureWorks Ingeo® 3052D (standard PLA) (second run). [Color figure can be viewed at wileyonlinelibrary.com]

degradation temperature (T_d) was assumed at 5% weight loss. All TGA results reported are single measurements.

Hot Fill Test

PLA (1A) and PP (Total PPC 5752) beakers were filled with boiling water. After 0, 1, 2, 3, 4, and 5 min a beaker was emptied and the dimensions of the beaker (height and diameter of the bottom of the beaker) were measured with a Profile Projector (Nikon, Amsterdam, the Netherlands). The percentage change in height or diameter was calculated, with reference being the dimensions before filling with hot water. Samples

were tested in duplicate and an average was calculated using Microsoft Excel.

Processing Parameters

The effect of higher mold temperatures was investigated by increasing the mold temperature from 30°C to 90°C. In addition, post-injection molding annealing of PLA (NatureWorks Ingeo® 3052D) was performed by placing the samples in an oven at 100°C during 10 min. Samples were cooled slowly (in the switched off oven).

RESULTS AND DISCUSSION

DSC

The DSC profile (second run) of NatureWorks Ingeo® 3052D (reference PLA) is shown in Fig. 1. A clear T_g and T_m (see also Table 4), both corresponding to the values mentioned on the technical datasheet, were observed, as well as a crystallization peak during heating (T_{cc}). This peak is very small, however, as is the enthalpic value of the melt peak. Together with the observed lack of a crystallization peak during cooling (T_c), this indicates a very limited crystallization, resulting in a mostly amorphous material. This was confirmed by the calculated percentage crystallinity, which was around 3% (second run) and can be explained by the intrinsic slow crystallization rate of PLA [26]. Indeed, the crystallization which did occur,

TABLE 4. Overview parameters DSC measurements.

Material	T_g (°C)	T_{cc} (°C)	T_c (°C)	T_m (°C)	X_c (%)
NatureWorks Ingeo® 3052D					
1st run	61.1	119.6	—	157.3	—
2nd run	60.9	122.8	—	155.3	0.5
Sabic PP 575P					
1st run	—	—	113.1	171.1	34.8
2nd run	—	—	108.8	167.1	40.9
NatureWorks Ingeo® 6400D					
1st run	62.4	104.1	—	173.0	5.7
2nd run	60.9	111.4	—	170.2	2.2
Stereocomplex PLA					
1st run	—	—	173.3/121.5	177.9/222.5	—
2nd run	—	—	165.3/126.1	175.5/219.9	—
PLA + fiber					
1st run	60.2	98.4	93.6	171.3	5.9
2nd run	61.5	—	93.8	168.4	22.9
PLA/PHB					
1st run	58.8	82.5	90.1	175.3	—
2nd run	63.2	—	85.2	164.2	—
PLA Ingeo® 3052D + Joncryl®FA 1009					
1st run	63.6	124.1	—	155.7	1.1
2nd run	61	127.3	—	152.4	0.2
PLA Ingeo® 3052D + Joncryl®FA 11005					
1st run	63.1	120.5	—	157.2	0.1
2nd run	61	122.2	—	153.4	0.6
PLA Ingeo® 6400D + Cloisite 15A					
1st run	60.9	94.6	—	171.9	8.8
2nd run	59.8	106.9	—	169.3	0.9
PHB					
1st run	—	—	—	177.9	28.2
2nd run	—	—	112.6	175	46.4
PHB + Joncryl®FA 1009					
1st run	—	—	—	179.5	21
2nd run	—	—	112.3	173.4	44.7

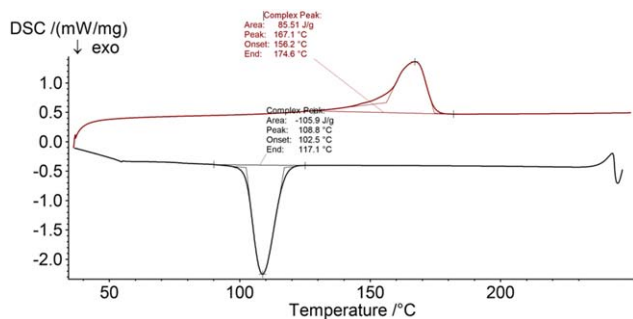


FIG. 2. DSC profile of Sabic PP 575P (standard conventional material) (second run). [Color figure can be viewed at wileyonlinelibrary.com]

happened during the reheating of the material and not during cooling, indicating that injection molded products might be fully amorphous after processing. A T_g within the temperature range of heat resistant packaging use, as is also described in literature [30], and a very low crystallization indicate that PLA is not suitable for applications where heat treatments are applied.

The DSC profile (Fig. 2) of Sabic PP 575P showed some big differences with the one of PLA. No T_g (T_g below zero, so outside the tested temperature range) or cold crystallization peak (T_{cc}) was observed. The T_m was around 165°C–170°C (Table 4), corresponding to literature [31], and during cooling a crystallization peak was detected (T_c), indicating good crystallization of the material. This was confirmed by the percentage crystallinity which was 40.9% (second run). These results indicate that PP has a good heat resistance and can be used for high heat packaging applications.

For stereocomplex PLA (sc-PLA), a similar DSC profile (Fig. 3) as the one of PP, with no glass transition within the tested temperature range, no crystallization peak during heating and a crystallization peak during cooling, was obtained, indicating better crystallization compared to pure PLA. Furthermore, two separate melt peaks were observed. The first melt peak originates from PLLA, while the second one originates from sc-PLA. The T_m of sc-PLA is higher than the T_m of the reference PLA. Because of the two melt peaks and the lack of information regarding the exact composition of the material, the percentage crystallinity could not be calculated. But the absence of a T_g within the tested temperature range, the higher T_m and the presence of a crystallization peak during cooling, pointing out good crystallinity, indicate that sc-PLA can probably be used for packaging applications undergoing a heat treatment step.

The DSC profiles (data not shown) of both the PLA + fibers and the PLA/PHB blend showed a lower T_{cc} (around respectively 98 and 83°C) and a higher T_m (respectively 171 and 175°C; Table 4) compared to the reference PLA. Both DSC showed a crystallization peak during cooling (Table 4), indicating a better crystallization potential of the material. The calculated percentage crystallinity of PLA + fibers were indeed improved (22.9%) compared to standard PLA (second run). Because of the double melt peak no percentage crystallinity of the PLA/PHB blend could be calculated. These results indicate a higher heat resistance of PLA + fibers and PLA/PHB compared to standard PLA. The higher crystallinity (PLA + fibers) or crystallization potential (PLA/PHB) can be explained because both the fiber surface and the PHB can act as a nucleating agent

in PLA [32, 33]. For the PLA/PHB blend, it was noted that the properties of both PLA and PHB were found in the profile, which suggests incompatibility between the two polymers. The compatibility of PLA and PHB is dependent on the molecular weight. According to Koyama and Doi [34] and Blumm and Owen [35] PHB is miscible with low molecular weight PLA ($M_w < 18,000$) in the melt, whereas PHB blends with high molecular weight PLA ($M_w > 18,000$) showed biphasic separation. Similarly, PLA is miscible with low molecular weight PHB ($M_w = 9,400$, up to 50 wt% PHB), but is immiscible with high molecular weight PHB according to Park et al. [36] and Ohkoshi et al. [37]. Since this was a commercial grade of which the composition was unknown it is possible that the molecular weights of PLA and PHB were incompatible. Furthermore, the T_m of the blend decreased with more than 10°C during the second heating cycle. This could indicate thermal degradation during processing, but it could also be caused by a different crystallization (due to cooling during the DSC measurement compared to cooling after processing) or a different contact surface compared to the first run.

The results of the DSC measurements show that the addition of the chain extenders Joncryl[®]FA 1009 and FA 11005 (2%) did not have a clear effect on the thermal parameters. The T_g , T_m , and T_{cc} (Table 4) remained more or less stable for respectively PLA, PLA + 2% Joncryl[®]FA 1009 and PLA + 2% Joncryl[®]FA 11005. Furthermore, the crystallinity (after the second run) of PLA + Joncryl[®]FA 1009 and of PLA + Joncryl[®]FA 11005 was also very low and comparable to neat PLA. This is probably because Joncryl[®] causes increased branching of the chains, leading to a more difficult alignment of the polymer chains. The decreased chain mobility normally results in a higher crystallization temperature during heating (T_{cc}), which was seen for Joncryl[®]FA1009, but not for Joncryl[®]FA11005 [38]. The addition of Cloisite 15A (5%) to PLA had no effect on the T_g and T_m of respectively PLA and PLA + Cloisite, but it did decrease the T_{cc} of PLA, indicating a better crystallization potential (broader window). This could be attributed to a nucleating effect of the nanoclay. In Table 4, this better crystallization potential can be seen after the first DSC run (8.8% vs. 5.7%) but not after the second run (0.9% vs. 2.2%), despite the decreased T_{cc} . Potentially, the shear-free heating of the polymer into melt phase during the DSC measurement could cause the Cloisite to coagulate. In extrusion, shear will forcefully cause the Cloisite to disperse and distribute throughout the melt. In the static conditions of the DSC apparatus, no such forces occur to overcome the thermodynamic tendency of the filler to coalesce into larger

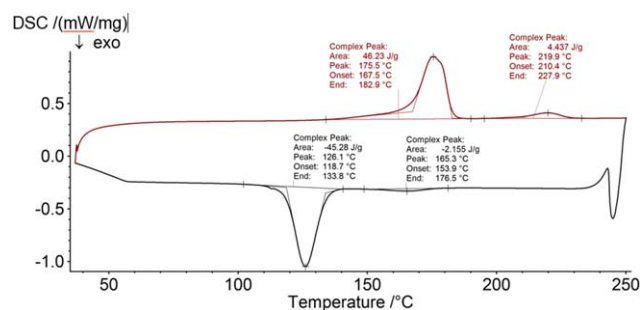


FIG. 3. DSC profile of Synterra[®] IM stereocomplex PLA (second run). [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 5. Overview vicat softening temperatures of tested materials.

Material	VST (°C)
Reference Ingeo 3052D PLA (12,2 N)	66.2 ± 1.4
Reference PP (12,2 N)	148.8 ± 0.6
PLA + fiber (12,2 N)	67.5 ± 0.4
PLA/PHB blend (12,2 N)	87.6
Sc-PLA (12,2 N)	152.7 ± 0.1
Reference Ingeo 3052D PLA (6.1 N)	57.9 ± 0.2
PLA + 2% Joncryl FA 1009 (6.1 N)	58.1 ± 0.7
PLA + 2% Joncryl FA 11005 (6.1 N)	57.7 ± 0.1
Reference Ingeo 6400D PLA (6.1 N)	56.1 ± 0.4
PLA + 5% Cloisite 15A (6.1 N)	52.9 ± 3.7
PHB (6.1 N)	154.8 ± 0.2
PHB + 2% Joncryl FA 1009 (6.1 N)	154.1 ± 0.1
PHB + 0.1% Hyperform [®] HPN 20E (6.1 N)	155.4 ± 0.3
PHB + 0.1% Hyperform [®] HPN 68L (6.1 N)	156.7 ± 0.3

domains. As 5% Cloisite is a rather large amount, this is a likely cause for the loss in nucleating effect between the first and second DSC run. As this seems to be a measurement artifact rather than an implication for the actual production of heat resistance-modified polymers, this hypothesis was not experimentally verified. Furthermore, no DSC measurements of the PLA + Hyperform HPN-20E[®] and Hyperform HPN-68L[®] were performed.

Based on the previous results of PLA + Joncryl[®], only 1 type of Joncryl[®] was added to PHB. The results of the DSC measurements of PHB and PHB + Joncryl[®]FA 1005 showed no T_g (around 5°C [39, 40], outside of the tested temperature range), no crystallization peak during heating, a melt peak and a clear crystallization peak during cooling. Both profiles were very similar but a slightly lower T_m and percentage crystallinity were observed after the addition of Joncryl[®]. This is because chain extenders increase the molecular weight by crosslinking or branching leading to a reduction in chain mobility [11]. The calculated crystallinity of PHB is lower than the percentage crystallinity described in literature [41].

Comparison of the DSC results of pure PLA and PHB leads to the conclusion that PHB is more heat resistant than PLA. DSC results of PHB are similar to the one of PP with only a melt peak and a crystallization peak during cooling (Table 4).

VST

The Vicat Softening Temperatures of sc-PLA and of PP were very similar (Table 5). The VST of PLA + fibers was similar to the VST of the reference PLA, while the PLA/PHB blend has an improved VST compared to neat PLA. These results also indicate that stereocomplex PLA has a good heat resistance, while the heat resistance of PLA + fiber and of the PLA/PHB blend has not (PLA + fiber) or only slightly (PLA/PHB blend) been improved compared to neat PLA. The increased crystallinity of the PLA + fiber did not result in a higher VST. This might be explained by the fact a higher crystallinity was only observed after the second run and the percentage crystallinity after the first run was similar to standard PLA. Furthermore, fibers have a reinforcing effect, which will probably have a clear effect on the HDT and less on the VST. The increased heat resistance of the PLA/PHB blend compared to standard PLA can probably be attributed to the higher heat resistance of

PHB. These results indicate that sc-PLA has a good heat resistance and that PHB intrinsically has also a good heat resistance, comparable to PP.

The addition of 2% Joncryl[®] masterbatch to PLA or PHB, the addition of 5% Cloisite 15A to PLA and the addition of the chain extender Hyperform[®] to PHB did not have a big influence on the vicat softening temperatures (VST) of the materials. This was expected, since the results of the DSC measurements already pointed out that these additives did not increase the heat resistance of PLA or PHB.

TGA

The results of the TGA measurements of PLA with and without Joncryl[®] showed that the addition of Joncryl[®] masterbatch resulted in a slightly higher degradation temperature (341.1°C for FA 1009 and 340.4°C for FA 11005) compared to the reference PLA (336.7°C). Also for PHB, a slightly higher (+2.8°C) degradation temperature was observed compared to the reference PHB. The improvements in degradation temperature by addition of the chain extender Joncryl[®] are limited and will only have a small effect during processing. This is in accordance with Najafi et al. [9], who found that out of several chain extenders, Joncryl[®] enhanced the degradation temperature the least. This can be explained by the fact that Joncryl[®] induces more branching in the polymer chain, increasing the molecular weight (positive effect on the degradation temperature), and also causing a high number of polymer ends (negative effect on the degradation temperature). The thermal degradation temperature of PLA decreased from 345.7°C to 334.9°C after addition of Cloisite 15A. This is in accordance to Meng et al. [16], Najafi et al. [9] and Wu et al. [17], who also found a decrease in degradation temperature after the addition of OMMT to PLA. No TGA measurements of PHB + nucleating agents were performed.

From all heat resistance tests, it can be concluded that, despite the higher T_m , the lower T_{cc} , and higher percentage crystallinity, the addition of fibers did not result in a better VST compared to standard PLA. The blending with PHB resulted in only a slight enhancement of the heat resistance with an increased T_m , increased percentage crystallinity and a higher VST. A reason for the poor improvement in heat resistance, which is in contrast with what was found in literature [25, 31, 42–44], could be a poor compatibility of the additives (fibers and PHB) with PLA. Stereocomplexation of PLA had the greatest effect on the heat resistance of PLA, with a clear increase in T_m and a much higher VST compared to standard PLA. The positive effect of stereocomplexation of PLA was also found in literature [22, 23]. The addition of the chain extender Joncryl[®] and the addition of Cloisite 15A did not improve T_g , T_m , T_c , T_{cc} , crystallinity and VST of PLA and/or PHB. But Joncryl[®] did have an effect during processing. PLA with Joncryl[®] had a higher and more stable viscosity compared to standard PLA, which was noticed because a higher pressure had to be applied at the second phase of injection (cooling and shrinkage in the mold). This higher viscosity can be explained by an increase in molecular weight by crosslinking and extension of the chains caused by the chain extender. The more stable viscosity is an indicator of less degradation. The more degradation products, the lower the viscosity. So, the higher and stable viscosity

TABLE 6. Effect of annealing on VST and HDT of different PLA and PP samples.

Material	VST (°C)	HDT (°C)
NatureWorks Ingeo 3052D (reference PLA)	66.2	46.2
Total PPC 5752 (reference PP)	153.1	41.0
13AO (PLA compound) (mold T -cooling t)		
30°C-90s	36.6	28.1
40°C-90s	138.5	29.4
60°C-90s	139.9	41.0
80°C-30s	136.7	38.4
14CC (PLA compound) (mold T -cooling t)		
40°C-60s	44.8	25.5
60°C-90s	137.0	29.3
100°C-60s	136.4	35.5

indicates that degradation during processing is reduced because of the chain extender [9, 10]. The addition of nucleating agent (Hyperform HPN[®]) slightly increased VST, but the VST of neat PHB was already very high. Furthermore, the DSC parameters and VST of PHB indicate that this material provides opportunities for heat resistant applications.

Processing Parameters

Annealing of NatureWorks Ingeo 3052D (standard PLA) had a clear effect on the HDT, which increased from 46.2°C to 59.1°C. The mold temperature during processing (and the inferred cooling rate from the melt) had a clear effect on the heat resistance of the material as well (Table 6). The Vicat softening temperatures of the 13OA PLA compound increased with over 100°C when a mold temperature of 40°C and more was used instead of a mold temperature of 30°C. A clear increase in HDT was seen as well. The Vicat softening temperatures of the 14CC PLA compound increased with over 90°C when a mold temperature of 60°C and more was used instead of a mold temperature of 40°C. For this PLA compound, a clear increase in HDT is seen as well. This can be explained by the fact that a higher mold temperature allows a slower cooling leading to a higher crystallinity of the PLA.

VST versus HDT

Table 6 also clearly shows that the VST measurements gave a higher value compared to the HDT measurements. Since both parameters are used to give an indication of the heat resistance, hot fill tests were performed with PLA (1A-131/14CC, mold $T < 40^\circ\text{C}$ and cooling time $< 60\text{s}$) and PP (Total) beakers to

TABLE 7. Change in dimensions (height and diameter) of PLA and PP beakers after filling with hot water (with reference being the dimensions before filling with hot water).

PLA Time (min)	% Decrease in		PP Time (min)	% Decrease in	
	Height	Diameter		Height	Diameter
1	6.64	0.37	1	-0.15	0.05
2	7.53	0.75	2	0.16	-0.01
3	8.12	0.77	3	0.10	0.07
4	7.50	0.36	4	0.06	0.07
5	8.01	1.63	5	0.06	0.07

check the reliability of both parameters. Immediately after filling (water temperature $\pm 93^\circ\text{C}$), a clear deformation of the PLA beakers was visually observed. The beakers became weak and difficult to hold. Furthermore, a reduction in optical clarity of the beakers was observed as well, indicating post-crystallization of the material. None of this was observed for the PP beakers. The deformation of the PLA beakers was confirmed by the measurements, as shown in Table 7. The beaker clearly shrank after filling with hot water (loss of height). Despite the observed softening of the PLA beaker no big decrease in the diameter was measured. This could be explained by the recrystallization of the beaker. The changes in height and diameter of the PP beakers before and after filling can be attributed to measurement errors. So despite the low HDT values (cfr. Table 6), the PP beakers do not deform when filled with hot water. It can be concluded that the HDT value does not always give a good indication of the functional heat resistance of a material. The VST values seem more reliable, but more research is necessary to draw a definite conclusion. The eventual use of the material is of course important as well.

CONCLUSIONS

From this research it can be concluded that the use of stereo-complex PLA, the use of higher mold temperatures for PLA or the use of PHB seems to provide the best opportunity as a rigid packaging material for food products that need to undergo a heat treatment. For all tested additives, the lack of (good) compatibility might be the reason for these poor results compared to literature. The addition of the chain extender Joncryl[®] did not affect the heat resistance of PLA or PHB, but it can be a solution to reduce the thermal degradation during processing. When comparing VST values with HDT values on the same material after hot fill testing, it seems that VST values were more reliable as heat resistant parameter for these kinds of applications.

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