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Enhanced crystallinity, toughness, and heat resistance of PLA using EVA, nucleating agent, and controlled crystallization

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Abstract

In this paper, we simultaneously improved the crystallinity, heat deflection temperature (HDT) and toughness of injection-molded poly(lactic acid) (PLA). We achieved this through the use of a nucleating agent (NA) and the impact modifier ethylene-vinyl acetate copolymer (EVA), and by in-mold crystallization (IMC) and post-production crystallization (PPC). The best results were achieved when 10 wt% EVA and 2 wt% NA were added to PLA, which was injection-molded into a cold mold and then annealed at 80 °C. In this case, the properties of the resulting PLA were very close to the properties of acrylonitrile-butadiene-styrene. In the case of IMC, the best results were obtained when PLA was modified with 20 wt% EVA and 2 wt% NA and crystallized in a mold at 90 °C. The main difference between the resulting properties of modified PLA subjected to IMC and PPC was in strain at break: 3.5 % for IMC and 14.6% for PPC. As the PLA-based compounds were crystallized by IMC and PPC, this huge difference between the strain at break of the samples can be explained with the differences in the crystalline structures developing under different conditions (crystalline modifications, spherulite size, etc.).

Keywords: Poly(lactic acid), crystallization, nucleating agent, ethylene-vinyl acetate copolymer (EVA), injection molding, impact modification

1. Introduction

The global problems of climate change, depletion of non-renewable natural resources, and plastic pollution, which human society has faced in the last few decades, led to a re-thinking of the traditional linear economy model [1]. As a result, society and industry, especially the polymer industry, are now moving towards sustainable development and a circular economy [2]. Plastics are essential to many aspects of sustainability due to their light weight and other beneficial properties. However, due to the high volume of production (more than 380 Mt yearly), the fact that most plastic is produced from petroleum, the large carbon footprint of manufacturing, and most degrade extremely slowly in the natural environment, plastics are very often not considered ecologically sustainable materials. A solution can be found in bio-based compostable plastics [3, 4]. Such materials are derived from renewable natural resources, exhibit a lower carbon footprint than petroleum-based polymers, and are biodegradable under particular conditions [5]. One of the most advanced and commercially available bio-based compostable plastics is poly(lactic acid) (PLA). The annual production of PLA reached 390 kt in 2020, which accounts for more than 18% of all bio-based plastics produced [6]. PLA is typically derived from crops that contain glucose (corn, wheat, rice, etc.) or saccharose (sugar beet, sugar cane, etc.). The properties of PLA, such as strength and stiffness, are comparable to or even superior to those of petroleum-based plastics, such as acrylonitrile-butadiene-styrene (ABS) and polypropylene (PP) [7]. After its useful life, PLA can be recycled or composted

under appropriate industrial conditions. However, its compostability strongly depends on factors such as molecular weight, crystallinity, additive content, and the size and shape of the product. While thin films often degrade within 60–90 days, larger injection-molded items may resist degradation or be rejected from composting facilities altogether [8–10].

Although PLA is already widely used for food packaging [11, 12] and tissue engineering [13, 14], its structural application in areas such as the automotive industry is now more the exception than the rule [15]. The reason is that despite some of its advantageous mechanical properties, such as high tensile strength and modulus, PLA has a relatively low heat deflection temperature (HDT) (~ 55 °C) and a low level of toughness [16]. Another shortcoming of PLA is when semi-crystalline PLA is used—it usually has better strength properties than amorphous PLA—its crystallization rate is relatively slow, which results in a fairly long injection molding cycle time (in the range of 5–10 minutes) [17]. Therefore, a lot of effort is put into adapting PLA for mass production and improving its shortcomings [7]. The toughness of PLA can be enhanced in various ways: with different additives, like plasticizers [18] and impact modifiers [19], by blending [20] and copolymerization [21] and (2) by mechanical modification techniques, such as stretching [22, 23]. The low HDT of PLA can be improved with fiber reinforcement [24], blending, or by increasing its crystallinity [25–27]. The last option is essential from the processing viewpoint, as process parameters, primarily mold temperature, can regulate the crystallinity of PLA. The crystallinity of injection-molded PLA can be improved either by post-production crystallization (PPC), also known as annealing [28], or by in-mold crystallization (IMC) with a mold temperature above the glass transition temperature (T_g) of PLA [29, 30]. Apart from processing conditions, the crystallinity of PLA is affected by its weight average molecular weight (M_w) [31], D-lactide content [32], and the presence of a nucleating agent (NA) [33]. The lower the M_w and D-lactide content of PLA, the higher its crystallinity is [34, 35].

Even though numerous methods exist to enhance the HDT and toughness of PLA, it is rather challenging to improve both of these properties simultaneously, while at the same time, other mechanical characteristics remain at an acceptable level and cycle time is also reduced. This balance can be partly achieved through the use of nucleating agents. These additives promote heterogeneous nucleation, accelerating crystallization and enabling higher overall crystallinity under identical processing conditions. As a result, a finer and denser crystalline morphology can be obtained, which contributes to improved thermal and mechanical performance. The enhanced toughness is likely related to the increased number of crystalline domains that serve as potential sites for stress transfer mechanisms such as shear yielding and interfacial debonding. At the same time, a higher crystalline fraction reinforces the PLA matrix, thereby improving its resistance to thermal deformation and leading to a higher HDT [36].

In our recent study [16], we showed that 2 wt% of an effective nucleating agent, such as zinc phenyl phosphonate (PPZn), Ecopromote[®] (Eco), or EcopromoteHD[®] (EcoHD), together with the hot mold (90 °C) effectively enhance the crystallinity and, consequently, the HDT of PLA, while reducing cycle time. We achieved a crystallinity of 44.5–50% depending on the additives and the thermal treatment, and the HDT of nucleated PLA increased from 55 °C to 88.8 °C. At the same time, nucleation and in-mold crystallization did not significantly increase the impact strength of PLA. Therefore, we investigated how the impact strength of PLA can be increased by adding a plasticizer while maximizing the crystallinity of PLA and improving its crystallization rate [37]. The plasticizers were oligomeric lactic acid (OLA) and dioctile adipate (DOA). We found that the HDT, tensile strength, and Young's modulus of PLA

improved with a nucleating agent and a plasticizer are even higher than those of ABS. However, the strain at break and the impact strength of the nucleated and plasticized PLA were still significantly lower than those of ABS. Therefore, in the current study we use another approach to improve the toughness of PLA—modification of injection-molded PLA with an impact modifier and nucleating agent, together with IMC or PPC (annealing).

Impact modifiers are elastomer-like materials that improve the toughness of polymers. Note that impact modifiers differ from polymer blends, where the latter is the mixture of several thermoplastics [7]. The most promising and available impact modifiers for PLA are natural rubber (NR) [38], ethylene-vinyl acetate (EVA) [39], and commercially produced impact modifiers like Elvaloy® and Biomax Strong®. Although all of these impact modifiers increase the impact strength of PLA, the effectiveness of each is different. For example, NR, when mixed with PLA, forms a droplet-like dispersed phase, and the adhesion between phases is rather weak, which leads to impaired properties [40]. Moreover, the size of the droplets highly depends on the amount of NR and the processing parameters, therefore the properties of modified PLA can vary in a wide range. Chen et al. [41] proved that above 10 wt% NR content, the strain at break of a PLA/NR blend significantly decreases, as too big NR droplets are formed in PLA. Elvaloy is an impact modifier produced by DuPont, and it is a terpolymer of ethylene, butylacrylate, and glycidyl-methacrylate (GMA). At least 30 wt% Elvaloy is needed to improve the strain at break of PLA [42]. However, while increasing in strain at break of PLA, Elvaloy considerably impairs the strength and modulus of PLA. BioMax Strong is another impact modifier produced by DuPont. It is an ethylene-acrylate copolymer (EAC). BioMax Strong effectively improves the ductility of low D-lactide content PLA, but it is not very effective for PLA with high D-lactide content [43]. EVA is a copolymer of ethylene and vinyl-acetate (VA). It is a thermoplastic elastomer with high flexibility and toughness. With the increase of VA content, EVA changes from a semi-crystalline low-density polyethylene (LDPE) into a rubber-like material and then into an amorphous poly(vinyl acetate) (PVAc) [44]. As PLA is miscible with PVAc while demonstrating a phase separation with LDPE, the compatibility of PLA and EVA can be regulated with the VA content of EVA. When VA content is between 40% and 70%, EVA demonstrates excellent compatibility with PLA and effectively increases its toughness. Tabi [45] discovered a positive synergistic effect in impact strength when EVA with 60% VA content was added to PLA and the PLA was then crystallized. He found that only 20 wt% EVA increases the impact strength of PLA from 2.3 to 8.7 kJ/m². The annealing of pure PLA increases its impact strength from 2.3 to 15.2 kJ/m² due to the improved crystallinity it produces. However, annealed PLA, which is also modified with 20 wt% EVA, demonstrates a superior impact strength of 65 kJ/m². Yeganeh and Moradi [39] also found that PLA with 25 wt% EVA (with 20 wt% VA) was effectively toughened when crystallized. The authors improved crystallinity with 10 wt% hydrophilic nano-silica and 5 wt% styrene-ethylene-butylene-styrene block copolymer grafted with maleic anhydride (SEBS-g-MA) block copolymer as compatibilizer. They reported that the notched Izod impact strength of PLA, which was modified with the nucleated agent and EVA, increased from 5.1 to 65 kJ/m². EVA acts not only as an impact modifier but also influences the crystallization behavior of PLA. Due to its partially miscible nature with PLA—depending on VA content—EVA can act as a soft, flexible dispersed phase and may serve as heterogeneous nucleation sites [46]. EVA increases the biodegradation rate of PLA by promoting water diffusion and increasing the amorphous fraction of PLA. On the other hand, even if EVA is biocompatible,

it is not a biodegradable polymer, so it remains a microplastic after the blends' decomposition [47-50].

Although the individual effects of nucleating agents, impact modifiers, and thermal treatments on PLA have been investigated previously, their combined and potentially synergistic influence has not been explored in a single systematic study. To address this gap, we designed an approach in which all three contributions are evaluated together.

In this study, after the previous attempt to simultaneously enhance the crystallinity, toughness, and heat resistance with plasticizer beside nucleating agent and crystallization, we use impact modifier instead of plasticizer to increase the crystallinity of PLA, its HDT, and toughness simultaneously by modifying it with an effective nucleating agent (EcopromoteHD) [16], and an impact modifier (EVA) as well as subsequent thermal treatment (IMC and PPC). The goal is to obtain a PLA-based material with a high renewable content and a property profile—particularly impact resistance and thermal performance—that exceeds the capabilities of currently available compostable PLA materials and reaches the performance range of fossil-based impact-modified polymers such as ABS.

2. Materials and equipment

2.1 Materials

The PLA used was 3100HP grade PLA (Nature Works, Minnetonka, MN, USA), which contains 0.5% D-lactide. Table 1 contains the properties of the PLA. Based on the producer's recommendations, PLA pellets were dried at 80°C for 5 hours before compounding.

Table 1. The properties of 3100HP PLA

Property	Unit	Value
Density	kg/m ³	1 240
Glass transition temperature (T_g)	°C	55–60
Melting temperature (T_m)	°C	170–190
Melt flow index at 210 °C, with a 2.16 kg load	g/10 min	22–24

The nucleating agent was EcopromoteHD (EcoHD), purchased from Nissan Chemical Industries Ltd. (Tokyo, Japan) and the impact modifier was Levapren 600 EVA (Lanxess, Cologne, Germany) with a VA content of 60%. The density of EVA was 1 040 kg/m³, and its Mooney viscosity was 27 MU.

2.2 Equipment for the production of specimens

For the compounding of PLA with EcoHD and EVA, we used a LabTech LTE 26-44 Scientific (Labtech Engineering Co., Ltd., Samutpreken, Thailand) (screw diameter = 26 mm, L/D = 40) twin-screw extruder. The temperature profile from the hopper to the die was 175–180–185–190 °C, and the screw rotation speed was 10 rpm. We added 2 wt% EcoHD, and 2, 5, 10, 15, and 20 wt% EVA to PLA. The extrudate compound was pelletized into 3 mm long pellets. The pellets were crystallized at 80 °C for 6 h.

PLA/EVA/EcoHD pellets were injection-molded with an Arburg Allrounder 370S 700–290 injection molding machine (Arburg GmbH., Lossburg, Germany). Screw diameter was 30 mm, and the length-to-diameter ratio of the screw was 25. Standard dumbbell

specimens were produced with a cross-section of 4 x 10 mm, in accordance with ISO 527-2/1-A. Table 2 contains the processing parameters.

For each blend, post-processing crystallization (PPC) was performed on injection-molded specimens originally produced in a 25 °C mold. The post-processing crystallization was conducted in a Faithful WGLL- 125 BE drying oven (Huanghua Faithful Instrument Co., Ltd., Huanghua, China) drying oven at 90, 100, and 110 °C. Prior to inserting the samples, the oven and a set of steel press plates—used for both heat transfer and mechanical stabilization—were preheated and maintained at the target temperature for at least 30 minutes. The specimens were then placed as quickly as possible between the hot plates in multiple layers, ensuring both sides of each sample were in full contact with a steel surface. This configuration served a dual purpose: it minimized deformation during the thermal treatment and facilitated rapid, uniform heating to the desired crystallization temperature. After 60 minutes of thermal treatment, the slightly softened specimens were removed and placed on a laminated wooden board to cool under ambient air. This ensured nearly flat geometry and uniform cooling of all samples.

In-mold crystallization (IMC) was performed by injection molding the PLA compounds directly into a hot mold of 90, 100 or 110 °C. As PLA was crystallized above T_g inside the mold, we use the term "in-mold crystallization time" instead of "residual cooling time". In-mold crystallization time was 90 s. Even though mold temperature was higher than the HDT of the just ejected PLA part, the crystalline structure of PLA ensured enough stiffness to demold the part properly.

Table 2. Processing parameters used for the production of injection-molded samples of PLA/EVA/EcoHD compounds

Processing parameter	Unit	PPC	IMC
Injection rate	cm ³ /s	50	
Holding pressure	bar	600	
Holding time	s	20	
Melt temperature	°C	190	
Residual cooling time/in-mold crystallization time	s	40	90
Mold temperature	°C	25	90; 100; 110
The temperature of the heat chamber	°C	90; 100; 110	not applicable
Time in the heat chamber	hour	1	not applicable

2.3 Equipment for the testing of specimens

The morphological characterization of the PLA/EVA/EcoHD compounds was performed with by differential scanning calorimetry (DSC), with a TA Instruments Q2000 (TA Instruments, New Castle, USA) device. The samples for DSC were cut from the middle of the injection-molded specimens. The weight of the DSC samples was 2–4 mg. The crystallization temperature (T_c), melting temperature (T_m), enthalpy of crystallization (ΔH_c), and enthalpy of fusion (ΔH_m) were determined with a non-isothermal regime "heat–cool–heat" from 0 to 200 °C with a heating and cooling rate of 5 °C/min. We calculated crystallinity (X) with Equation (1).

$$X = \frac{\Delta H_m - \Delta H_c}{\Delta H_f \cdot (1 - \alpha)} \cdot 100\%, \quad (1)$$

where ΔH_f is the enthalpy of fusion for 100% crystalline PLA (93.0 J/g) [51], and α is the mass fraction of the additives (EVA and EcoHD). Due to the very small amount of post-crystallization observed in the samples, the baseline after the glass transition was not sufficiently well defined. Consequently, T_g values could not be determined with the accuracy required for meaningful structural interpretation.

We determined the tensile properties and impact strength of PLA/EVA/EcoHD specimens. Tensile tests were performed on a Zwick Z020 universal testing machine (UTM) (Zwick, Ulm, Germany) equipped with a Zwick BZ 020/TN2S force cell. Tensile tests were conducted in accordance with ISO 527. Crosshead speed was 5 mm/min. The Charpy impact tests were performed with a Ceast Resil Impactor (Ceast, Torino, Italy) machine, with a 15 J impact energy hammer. Notched specimens were used in the impact tests, according to ISO 179. The tests were performed at room temperature in a relative humidity of $50 \pm 10\%$. Six samples were tested in each test. The standard deviations were plotted as error bars; however, in most cases they are not visible because they fall within the size of the marker symbols.

The HDT of PLA/EVA/EcoHD was measured with a Ceast HV3 HDT (Ceast, Torino, Italy) device. The HDT B test was conducted according to ISO 75. Span length was 64 mm, loading stress was 0.45 MPa, and the heating rate was 2 °C/min (120 °C/hour). When the deflection of a sample reached 0.34 mm, the HDT test was stopped. Three specimens were used in the HDT test.

3. Results and discussion

3.1 Crystalline properties of the injection-molded PLA/EVA/EcoHD compounds

The DSC heating curves show that cold crystallization was considerably reduced as a result of the post-treatments, in fact, it is almost negligible. (Figure 1 a). If we look at crystallinity, we get a much more detailed picture of the combined effects of the nucleating agent, EVA content, and the heat treatment (Figure 1 b). A 5 wt% EVA content resulted in a notable increase in the crystallinity of the non-heat-treated material without a nucleating agent. However, at higher concentrations, a slight decrease was observed, followed by a plateau (Figure 1b; line labeled PLA+EVA_not crystallized). A slight increase in crystallinity was observed in PLA/EVA blends without nucleating agent, which can be attributed to local interfacial thermal effects. During PLA crystallization, the released heat partially dissipates into the amorphous EVA domains, reducing self-heating in the adjacent PLA regions. As a consequence, metastable nuclei are less likely to redissolve compared to the bulk PLA, allowing slightly more stable crystal structures to form in the vicinity of EVA. When there was also a nucleating agent in the system, crystallinity increased further, here a slight decreasing trend can be observed with increasing EVA content. In other words, the nucleating agent worked well.

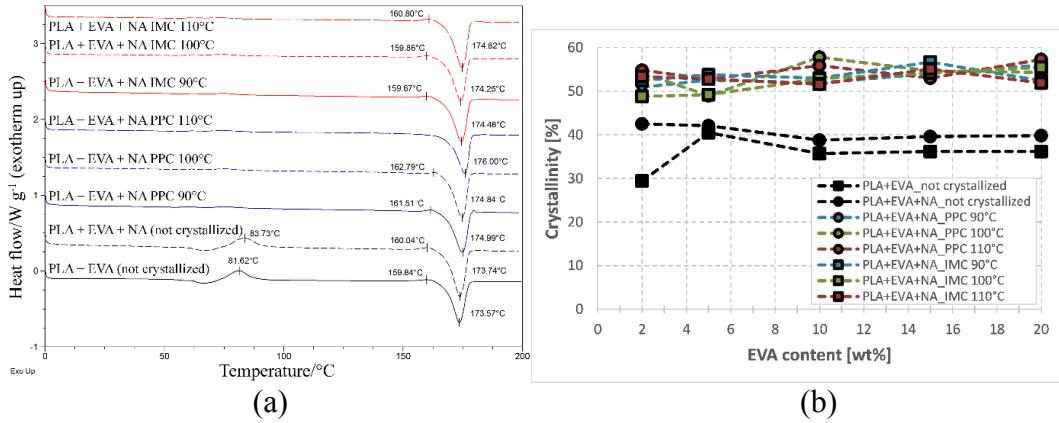


Figure 1. Results of DSC: (a) The first heating scans of the materials produced; (b) crystallinity calculated from the first heating.

Both the crystallization in the mold and the subsequent heat treatment increased the crystallinity significantly. When we consider a given heat treatment, the trends with increasing EVA content are not clear, this results from the small sample mass, as such a small mass cannot be expected to accurately represent nominal EVA content. Nevertheless, when we look at all the heat-treated samples, a small but definite increase in the crystalline fraction can be observed with increasing EVA content.

3.2 Mechanical and heat deflection properties of the PLA/EVA/EcoHD compounds

We examined the mechanical properties of the materials produced (Figure 2). An increase in EVA content reduced both tensile strength and the tensile modulus of elasticity. This result was expected, since both the strength and modulus of EVA are lower than those of PLA. The question here was to what extent this reduction can be compensated for with crystallinity-increasing methods. These did not change strength significantly, but they changed modulus significantly. This difference in properties is probably due to the fact that in the case of tensile stress, the softening effect of EVA is dominant at large deformations, while at small deformations, where the modulus is calculated, there is better load transfer between the phases, so the higher modulus of PLA resulting from its higher crystallinity was decisive in the mixture. Also, IMC was more effective than PPC.

A slight increase in strain at break was observed with increasing EVA content in the samples without nucleating agent and without crystallization. Up to 15 wt% EVA, the average strain at break increased; however, the standard deviations were large (Figure 2 c). Despite the increased strain at break, no improvement in impact resistance was observed, as will be shown later. In samples containing nucleating agent or subjected to thermal post-treatment, the effect of EVA on strain at break was less pronounced; however, under these conditions, some PPC-treated PLA/EVA blends still showed moderately improved values, particularly at 100 and 110 °C, compared to neat PLA, which typically exhibits a strain at break of ~5% under similar processing conditions [37]. Increasing the crystallization temperature led to a decrease in the strain at break of the PLA compounds, and samples crystallized in the mold (IMC) exhibited lower strain at break values than those subjected to post-processing crystallization (PPC). These findings suggest that EVA may slightly increase the strain at break in certain cases, particularly when a nucleating agent is present.

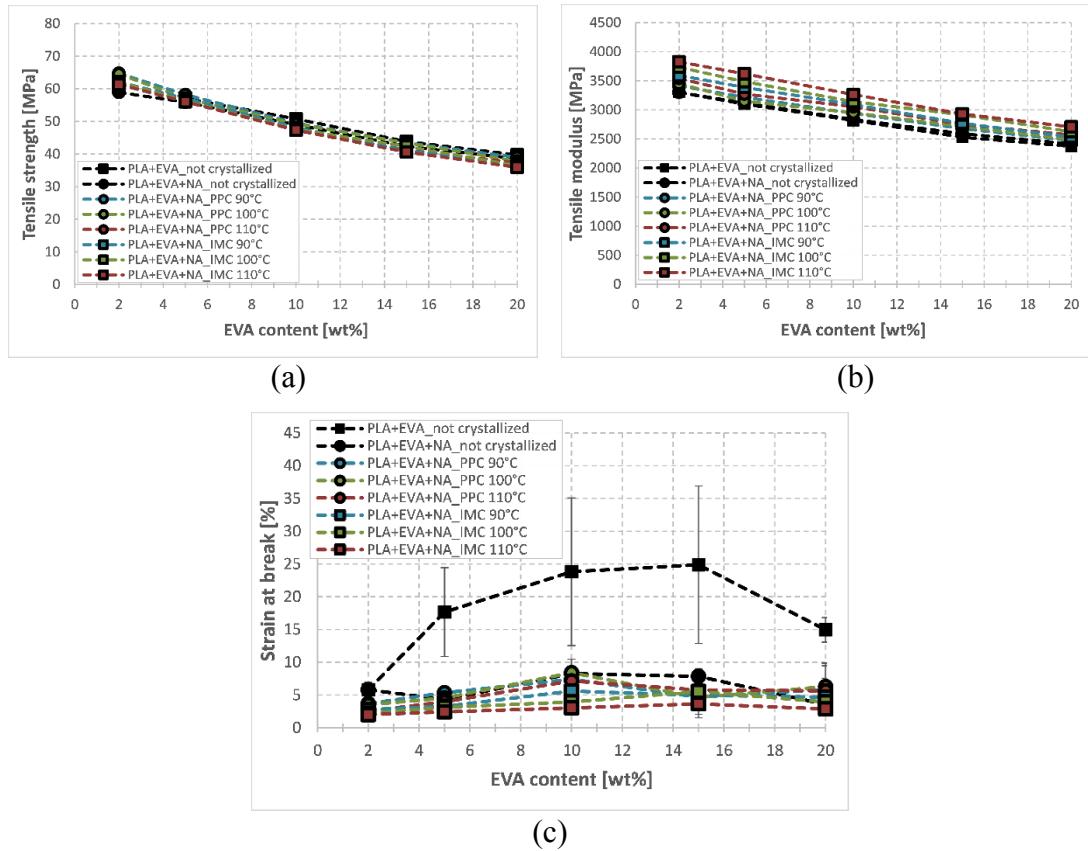


Figure 2. (a) Tensile strength; (b) tensile modulus; (c) strain at break of the in-mold crystallized and annealed PLA/EVA/EcoHD compounds.

The Charpy impact strength of PLA-based compounds increased with increasing EVA content (Figure 3). A positive toughening cross-effect between EVA and IMC-induced improved crystallization. An impact strength of 35 kJ/m^2 was achieved when 20 wt% EVA and IMC at 90°C were used together. However, this result is lower compared to what was achieved with PPC. Moreover, impact strength decreased with an increase in crystallization temperature, and even more moderate results were achieved when IMC was used instead of PPC. This is unfortunate since IMC can be considered part of injection molding, while PPC is an additional, time-consuming post-production step. This difference in properties is probably due to the differences in crystallites of PLA that develop when it is subjected to post-production crystallization or in-mold crystallization. Although DSC measurements showed comparable melting temperatures and overall crystallinity for IMC- and PPC-treated samples, the distinct thermal histories likely resulted in different crystalline morphologies. During IMC, rapid cooling and high thermal gradients may favor heterogeneous crystallization, leading to a more crystalline outer layer and a less crystalline core [52]. In contrast, the slower, uniform heating during PPC allows for more homogeneous bulk crystallization. These differences can influence internal stress distribution, spherulite size, and crystal perfection, ultimately affecting mechanical performance [53].

In the case of semi-crystalline polymers, increased supercooling favors nucleation over crystal growth, leading to the formation of numerous, smaller crystallites [54]. As a result, IMC conditions tend to produce smaller and more numerous spherulites, especially near the mold surface. Although PPC involves heating rather than cooling, the trend remains similar: lower crystallization temperatures still favor nucleation over growth. This mechanism may explain

why samples post-crystallized at 90 °C exhibited superior mechanical performance within the PPC group. The finer, more uniform crystalline morphology likely provided better stress distribution and reduced the risk of localized failure, despite the bulk crystallinity being comparable to that of other PPC samples. This trend was particularly evident in samples containing 20 wt% EVA, where the highest impact strength was observed at 90 °C crystallization. This suggests that the finer, more uniform crystalline morphology at lower crystallization temperatures enhanced the effectiveness of EVA toughening mechanisms, such as shear yielding or debonding [36].

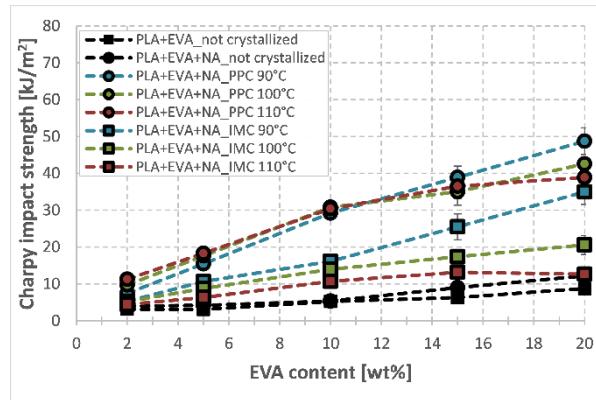


Figure 3. Charpy impact strength (g-h) of the in-mold crystallized and annealed PLA/EVA/EcoHD compounds.

The synergistic improvement in impact resistance observed in the PLA/EVA/EcopromoteHD blends can be explained by the combined effects of crystallization-induced microstructural refinement and EVA-assisted energy dissipation. The presence of the nucleating agent increases the nucleation density and leads to the formation of smaller and more uniformly distributed spherulites, which enhances stress distribution and increases the effective fracture path during loading, in accordance with earlier observations in semi-crystalline PLA systems [25–27, 54]. At the same time, EVA contributes through established toughening mechanisms such as shear yielding and interfacial debonding, whose efficiency is known to be higher when the matrix exhibits finer crystalline morphology and improved homogeneity [36, 39, 44]. Previous work has already indicated that PLA crystallinity can significantly amplify the toughening effect of EVA [45], supporting the interpretation that the microstructure generated under IMC or PPC conditions facilitates more effective activation of these mechanisms. Consequently, the improved impact performance arises not simply from the additive contributions of EVA and crystallization, but from their mutually reinforcing interaction.

Based on these observations, a straightforward structural model can be proposed to explain the synergistic improvement in impact resistance. Without nucleation and post-crystallization, PLA is essentially brittle: a crack progresses quickly and practically without obstacles (Figure 4 a). As a result of crystallization, the spherulites that form produce a barrier (Figure 4 b), which is manifested in an increase in the length of the fracture path, and thus the energy absorbed during fracture increases. This energy can be further increased if a nucleating agent is added to the material, because then the growth of spherulites starts from many points; average spherulite size decreases, which further increases the length of the fracture path (Figure 4 c). If the rubbery, highly absorbent EVA is also present, the crack may even get stuck at this stage—

far more energy is needed for fracture (Figure 4 d). These four microstructural states represent successive levels of resistance against crack propagation: from an unobstructed brittle path, through increasingly tortuous routes created by crystallization and nucleation, to a morphology where EVA domains introduce additional local energy dissipation by deforming or triggering debonding processes.

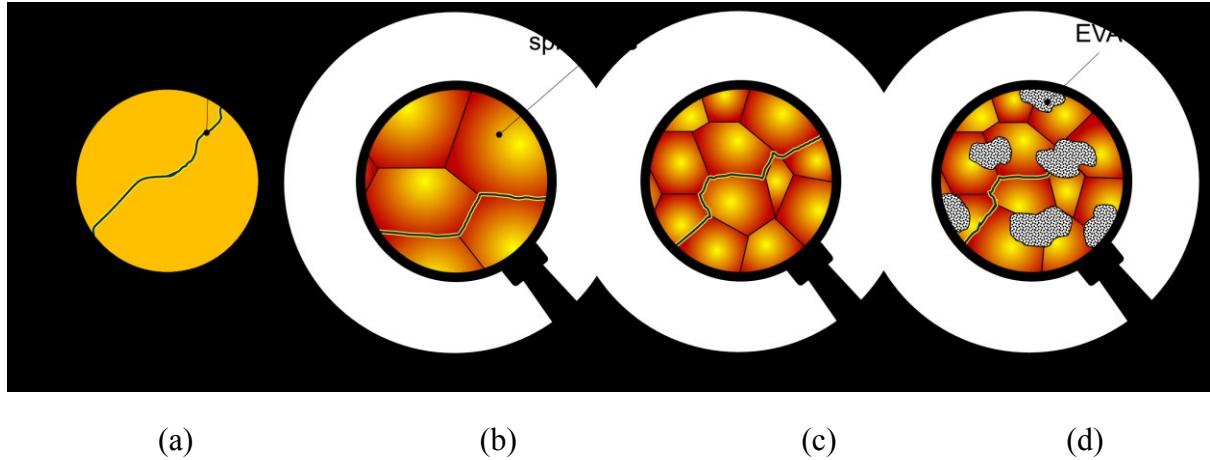


Figure 4. The microstructure of PLA: (a) without annealing and nucleation; (b) large spherulites as a result of annealing, (c) the spherulites are smaller as a result of nucleation and annealing, (d) with annealing, nucleation and EVA “islands”.

In addition to these structural effects, weak interfacial interactions also contribute to the mechanical response of the blends. Although no new chemical bonds are formed, the carbonyl groups of PLA and the vinyl acetate units of EVA exhibit mild polar affinity, and the surface of the nucleating agent particles interacts weakly with the surrounding PLA chains. These secondary interactions do not alter the overall morphology, but they improve local stress transfer and facilitate the activation of EVA-based energy dissipation mechanisms, such as shear yielding or interfacial debonding. Furthermore, these interfacial interactions are consistent with the slight crystallinity increase observed in PLA/EVA blends without nucleating agent, where the EVA domains locally buffer the heat released during crystallization, aiding the stabilization of otherwise metastable nuclei. This subtle interfacial influence on crystallization complements their mechanical role, reinforcing the overall structure–property relationships described above.

Beyond crystallization-induced effects, property changes related to shrinkage must also be considered. The thermal expansion coefficient of EVA (~300 ppm/K [55]) is higher than that of PLA (~80 ppm/K [56]). Of course, there is a difference in their dependence on temperature. Also, in the case of EVA, the thermal expansion coefficient is influenced by the amount of vinyl acetate, while in the case of PLA, it is influenced by D-lactide content, but the difference is fundamentally significant. This difference means that when the PLA is amorphous, the connection between the phases is not particularly good. However, according to the datasheet of PLA, crystallization results in significant shrinkage: it is approximately 1.5% higher compared to amorphous PLA.

Summarizing the structure–property relationships, the mechanical performance of the PLA/EVA/EcoHD blends can be directly traced back to the microstructural features formed

through nucleation, EVA toughening, and controlled crystallization. The increased nucleation density and the resulting finer, more uniformly distributed spherulites enhance stress distribution and extend the fracture path, while EVA introduces energy-absorbing domains that activate shear yielding or debonding under impact. Although IMC and PPC yield similar overall crystallinity, their distinct thermal histories result in different crystalline morphologies; smaller and more homogeneous spherulites formed at lower crystallization temperatures significantly improve the efficiency of EVA-assisted toughening. As a combined effect, the blends exhibit a microstructure capable of efficient energy dissipation and delayed crack propagation—features characteristic of high-performance impact-modified polymers. Overall, we obtain a material with good impact resistance properties and very similar in structure to ABS.

Figure 5 shows the HDT of the crystallized PLA/EVA/EcoHD compounds. We found that without crystallization, the HDT of the nucleated and impact-modified PLA does not change with increasing EVA content. Crystallization is necessary for an increase in HDT.

When PPC or IMC was applied, the resulting enhanced crystallinity greatly increased the HDT of PLA. The higher the crystallization temperature was, the higher HDT was. Moreover, HDT was higher when IMC was used instead of PPC. The presence of EVA had a negative influence on the HDT of PLA, as was expected. However, most of the examined compounds had a higher HDT than ABS GP35 ($\sim 95^\circ\text{C}$).

Although impact strength decreased with increasing crystallization temperature, the HDT values followed the opposite trend. This behavior can be explained by the distinct roles of crystalline morphology in thermal and mechanical performance. At higher crystallization temperatures, slower nucleation and enhanced crystal growth result in larger and more perfect crystallites. These structural features increase the dimensional stability of the PLA matrix, improving heat deflection resistance. In contrast, finer and more uniformly dispersed crystallites—typically formed at lower crystallization temperatures—enhance impact performance by reducing internal stress concentration and promoting energy dissipation through toughening mechanisms. Therefore, the observed divergence in HDT and impact strength trends is consistent with the underlying structure–property relationships.

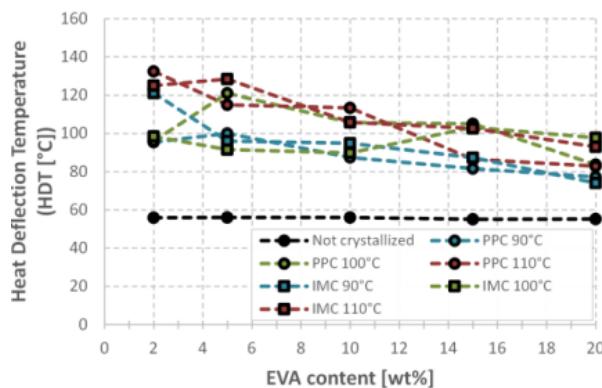


Figure 5. The HDT of the crystallized PLA/EVA/EcoHD compounds

We found the best compromise between the mechanical and thermo-mechanical properties of PLA-based compounds when 20% EVA and 2 wt% EcoHD were used, together with a hot mold at 90°C . Under these conditions, the PLA+20%EVA+NA compound had mechanical and thermal properties very similar to those of BASF Terluran ® GP-35 acrylonitrile-butadiene-styrene (ABS GP35) (Table 3). It is notable that the Charpy impact

strength is far higher than that of ABS, but the HDT is lower. Among the materials we produced, there is one whose HDT is higher than that of ABS GP35, but it has lower impact strength. We consider this material a good competitor because an HDT of 75 °C is high enough for engineering applications. Typical ABS applications include housings and casings for small electronic devices (e.g., chargers, handheld tools, sensors), appliance components, interior technical parts, and various consumer-product enclosures. Based on its mechanical and thermal performance, the developed PLA/EVA/EcoHD material approaches the property range required for such applications and may be considered a potential candidate for similar non-load-bearing structural parts, small housings, protective covers, or technical casings where a higher bio-based content is desired.

Table 3. Comparison of the properties of the PLA+20%EVA+NA compound crystallized in a mold at 90 °C and the properties of ABS GP35

Property	Unit	PLA+20%EVA+NA_IMC90°C	ABS GP35
Tensile strength	MPa	37	44
Tensile modulus	MPa	2 530	2 300
Strain at break	%	4.7	15
Charpy impact strength	kJ/m ²	35	19
HDT	°C	75	95

4. Conclusions

In this paper, we examine how much we can modify the mechanical and thermo-mechanical properties of injection-molded PLA. The properties of ABS were considered a benchmark. It is well-known that pure, unmodified PLA outperforms ABS in terms of tensile strength and modulus, while in terms of strain-at-break, impact resistance, and HDT, PLA is greatly inferior. To enhance these weak properties of PLA, we selected the PLA with the lowest possible D-lactide content, and modified it with the most effective nucleating agent, EcoHD, and an effective impact modifier that has a positive cross-effect with the improved crystallinity of PLA. To increase the crystallinity of PLA, we used two methods of thermal treatment: crystallization in a hot mold (also called in-mold crystallization, or IMC), and annealing (also known as post-production crystallization, or PPC). We found that when 10 wt% EVA and 2 wt% EcoHD were added to PLA injection-molded into a cold mold and then annealed at 80°C, the properties of the resulting material were very close to (or even outperformed) the properties of ABS. For example, the tensile strength and modulus, as well as the strain at break of the modified and annealed PLA are almost the same as those of ABS. At the same time, the Charpy impact strength of the modified PLA is almost three times higher than that of ABS (53.7 and 19.0 kJ/m² for the modified PLA and ABS, respectively). The HDT of the modified PLA was still lower than the HDT of ABS (78.8 °C and 95 °C respectively). However, the HDT of PLA increased significantly due to the above-mentioned modifications and thermal treatments, and can therefore be considered acceptable.

Even though PPC is an effective method to increase the crystallinity, and thus the HDT of PLA, the cost of this improvement was the warping of PLA products during PPC. Another problem with PPC is that it is an additional and time-consuming post-production step, which

is undesirable in injection molding. Therefore, we also examined the possibility of using IMC to increase the crystallinity of PLA, which is preferable as IMC is considered a part of the injection molding production process. The best results in terms of mechanical properties were produced when PLA was modified with 20 wt% EVA and 2 wt% EcoHD and crystallized in a mold at 90°C. In this case, the tensile strength of PLA was a little lower than that of ABS (38 and 44 MPa, respectively), but the tensile modulus of PLA was higher than that of ABS (2700 and 2300 MPa, respectively). The Charpy impact strength of modified PLA was almost double that of ABS (35 and 19 kJ/m²), while the HDT of modified PLA was lower than that of ABS (75 and 95 °C). Unfortunately, the strain at break of modified and in-mold crystallized PLA was only 3.5%, which is considerably lower than the strain at break of ABS, which is 15%. We found that independently of the thermal treatment (PPC or IMC), the PLA-based compounds fully crystallized, and the maximum possible crystallinity (in the range of 55–58%) was achieved. Therefore, the considerable difference between the strain at break of the samples produced with IMC and PPC is most probably caused by the differences in the crystal structures that developed under the different conditions (crystal modifications, spherulite size, etc.).

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Author contributions

G. Cs. performed the data analysis and visualization, and contributed to the preparation of the original draft. L. M. was responsible for data curation and formal analysis, and also contributed to the preparation of the original draft and visualization. T. T. contributed to the conceptualization and methodology, supervised the work, and also participated in the preparation of the original draft. All authors reviewed the manuscript.

Conflicts of interest

The authors declare no conflicts of interest.

Data and code availability

The datasets generated and analyzed during the current study are available from the corresponding author on reasonable request.

Supplementary information

Not applicable.

Ethical approval

Not applicable.

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