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On the Cryo-Molding Process and Subsequent Forming Processes of Biopolymers with Low Glass Transition Temperature

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On the Cryo-Molding Process and Subsequent Forming Processes of Biopolymers with Low Glass Transition Temperature

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Abstract: Bio-based as well as biodegradable polymers are increasingly finding their way into applications such as food packaging. Here, certain biopolymers with a high degree of crystallinity may be of interest due to their superior barrier properties. Conversely, forming processes including high deformations often require an almost amorphous material state to avoid the brittle behavior associated with crystal structures. For some of those biopolymers, the narrow window in which they can be processed has delayed their potential use for packaging applications. In rigid packaging, two-step processes are commonly used for the production of containers from thermoplastic polymers. These processes, such as thermo forming or injection stretch blow molding, are a combination of a conversion step, e.g. film extrusion or injection molding, and a deformation step. However, to enable a forming process, the material properties after the first (conversion) step need to fulfil the mechanical requirements of the forming process. For semi crystalline polymers, these requirements are closely linked to the morphology of the converted material. A new process is presented to prevent crystallization and allow for a subsequent forming step. The efficiency of this process is evaluated on tailored lab scale equipment. This publication will provide insights into the opportunities as well as potential challenges presented by the "Cryo-Injection-Molding" (CIM) process. The CIM uses a mold that is cooled by liquid nitrogen. This mold is insulated and used in a lab scale injection process. This process is capable of cooling specimens down to their amorphous state (or semi-crystallin state with a very low degree

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of crystallinity) and allows the mechanical characterization in a softened state at a temperature above glass transition. To prevent unintended changes of the morphology, after the production process, the samples are stored at a temperature below glass transition and later heated using custom convectional heaters in a setup of a tensile testing machine. In this context, PBAT, PBS and PHA biopolymers are tested exemplarily.

Keywords: Cryo-Molding, Injection Molding, CIM, Morphology, Amorphous, Biopolymer, Processing, PHA, PBAT, PBS

Introduction

Packaging materials must fulfill many requirements, including mechanical and chemical requirements, with the product's shelf life being one of the key performance indicators. The packaging shelf life is also linked to the barrier of the packaging material. Typically, water vapor and gases like oxygen and carbon dioxide should be blocked.

In general, for many thermoplastic packaging materials, this barrier depends on the degree of crystallinity i.e. poly(ethylene terephthalate) (PET) [1]. An increase of crystallinity thereby leads to improved barrier properties, among other effects, due to an increased packing density leading to a reduction of free volume [2]. In contrast, high crystallinity will prevent materials from being easily formable. This causes technical challenges in two stage processes like thermoforming or injection stretch blow molding (ISBM). In thermoforming as in ISBM the morphology of the precursors can define the processability. A high degree of crystallinity in those precursors will prevent the downstream processability, since large deformations might no longer be reached.

This conflict between high barrier and good formability can potentially be resolved by the decomposition of both requirements by avoiding the formation of crystalline structures for the time until the final packaging shape is reached. This approach is investigated by processing bio-based thermoplastics that differ in their crystallization rate and formability.

Materials

The investigated materials are biopolymers that are made from bio and fossil-based sources and are categorized as biodegradable [3]. Commercial grades were used, to access processable amounts for the specimen production. The used material grades are listed in Table 1.

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Table 1. Materials used in this investigation.

	Supplier	Application	Similar conventional plastics	Source / Degradability
PBAT Polybutylene adipate terephthalate				
Ecoflex® F Blend C1200	BASF	Blown Films, Cast Film	LDPE	Fossil based / Biodegradable
PHA (polyhydroxyalkanoates)-based thermoplastic				
ErcrosBio® PH 110	Ercros	Injection Moulding	Mechanical: LDPE Barrier: PET Haptic: PP	Bio based / Biodegradable
PBS Bio-based polybutylene succinate				
BioPBS™ FZ91PM	Misubishi Chemical	Blown Films, Cast Films	LDPE	Bio based / Biodegradable

To identify the mechanical behavior of amorphous biopolymers, three materials with low glass transition temperature are studied. Their low glass transition temperature suggests that they crystallize at room temperature, making their amorphous behavior previously unknown. PHA, PBAT, and PBS are selected to showcase the bandwidth of processability. PHAs are difficult to use in forming processes, due to their brittleness, associated to spherulitic crystallization [4]. PBAT and PBS are suitable for conventional forming processes due to their high maximum strains [5]. All of these materials are compared by their processing and mechanical properties with LDPE.

For semi-crystalline thermoplastic materials, the cooling rate has an influence on the degree of crystallinity when cooling from the molten state. The effect of two different cooling rate on the crystallization enthalpy, as measured by DSC, are given in Table 2.

Table 2. Selected thermal properties of PHA, PBS and PBAT.

Material	Tg (°C)	Tm according to TDS (°C)	Relative change in Crystallization Enthalpies (10 K/min vs. 100 K/min, DSC) (%)
PBAT	-29.2	110–120	-19.2
PHA	-1.8	124	-15.5
PBS	-34.9	115	-15.5

An increase of the cooling rate from 10 K/min to 100 K/min in DSC measurements yields a significant reduction (>15%) in the recrystallisation peak. The crystallinity can be further suppressed by increasing the cooling rate. For the injection molding process, this is tested by minimizing the mold temperature by using liquid nitrogen.

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Process

The method of changing the morphology for precursors in forming processes allows reconsideration of the thermal history of the processing of biomaterials. In Figure 1, a possible temperature history for the novel CIM process is presented schematically.

The CIM process is characterized by an injection process above the specific melt temperature of the material, followed by cooling at mold temperatures at around -100°C. After demolding the specimens at that temperature, the specimens are kept cold by keeping them in liquid nitrogen, or a deep freezer at approximately -80°C.

Due to the expected low degree of crystallinity, it is assumed that the material will become formable once reheated to temperatures above glass transition. Therefore, in the subsequent process step the material is reheated to temperatures above the glass transition. This is indicated for the bio polymers with temperatures above 0°C in Figure 1. To assess the mechanical behavior of the material at those temperatures, the heated specimens are immediately subjected to tensile testing. This uniaxial testing mimics a subsequent forming process and makes it possible to study the formability of the material in its amorphous condition. Finally, the specimens rest at environmental conditions to slowly recrystallize. During the forming process, this recrystallization could assist a formed packaging in achieving the required specifications, due to a greater stiffness of the recrystallized material and to possibly enhanced barrier properties of the same.

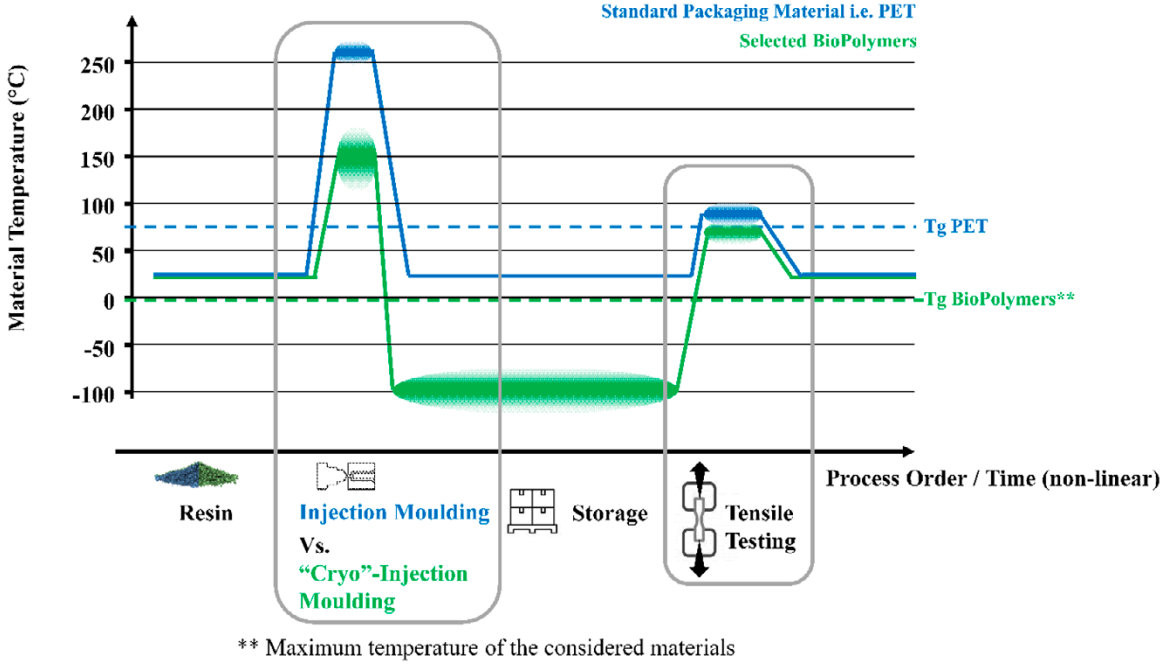

Figure 1. Schematics to compare the thermal history of the processing–Biopolymers vs. PET.

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Specimen Production with the Use of "Cryo-Injection-Molding"

The CIM process uses a custom build tool, that can be used in conjunction with a commercially available micro compounder (Xplore MC 15 HT & IM 12). The "cryo"-tool contains a cavity for an ISO 527 type "1BA" specimen. The cooling mechanism is realized by two open cooling circuits that use the negative pressure created by two venturi pumps to slowly transfer the liquid nitrogen into the molds. An excerpt of a resulting temperature evolution of the mold during testing can be seen in Figure 2.

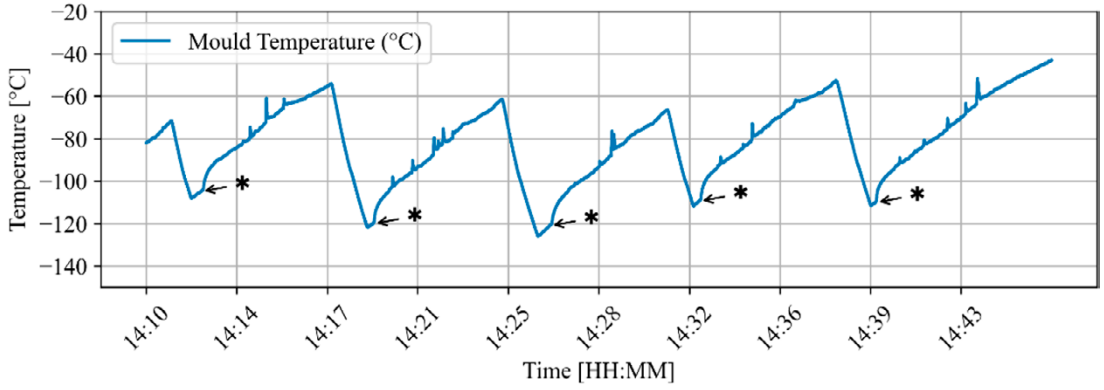

Figure 2. Mold temperature during the injection. The * indicates the time of the injection.

Due to the manual valve opening and closing, the temperature of the mold is oscillating between 40°C and 130°C. The injection process starts after cooling down the mold and reaching temperatures below -100°C. At that temperature, the mold heats up about 9 K due to the injection of the hot polymer. This shows that the thermal mass of the mold is dominant, compared to the thermal mass of the specimen. The unmolding begins right after the injection and the specimens are transferred into the cold storage.

Due to the extreme low temperatures on the mold surfaces and parting plane, humidity condenses on theses surfaces and thin ice layers occur. At some point the extensive ice on the parting surfaces leads to non-closed mold and therefore to flashing.

In conventional processes the used PHA type must be kept in the mold for about 60 seconds at 60°C or higher. The resulting crystallization is needed, since otherwise the polymer at that stage is too soft to be ejected by most ejection systems. Additionally, in the conventional process the material is very sticky to the mold surfaces, as long it is not crystallized. It was observed that this stickiness is avoided below its glass transition temperature in the CIM process. At the low temperatures these biomaterials can be demolded easily and right away. This could lead to an economic advantage due to shorter cycle times in the processing of PHA and other biopolymers.

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Evaluation of the Mechanical Properties by Tensile Testing

Since these materials' glass transition temperatures are well below environmental temperatures and they recrystallize at those temperatures, their behavior in their amorphous state is still unknown.

To quickly and reliably heat up the tensile specimens, a convectional heating device is used to heat up the specimens from both sides. The actual temperature of the specimens right before the deformation with 1000 mm/s is evaluated using thermal imaging technology.

In Figure 3, the specimens made of PBS and PBAT show similar results for both processes, for the CIM and for the regular injection molding. Still, the CIM materials break at larger strains and show overall lower stresses.

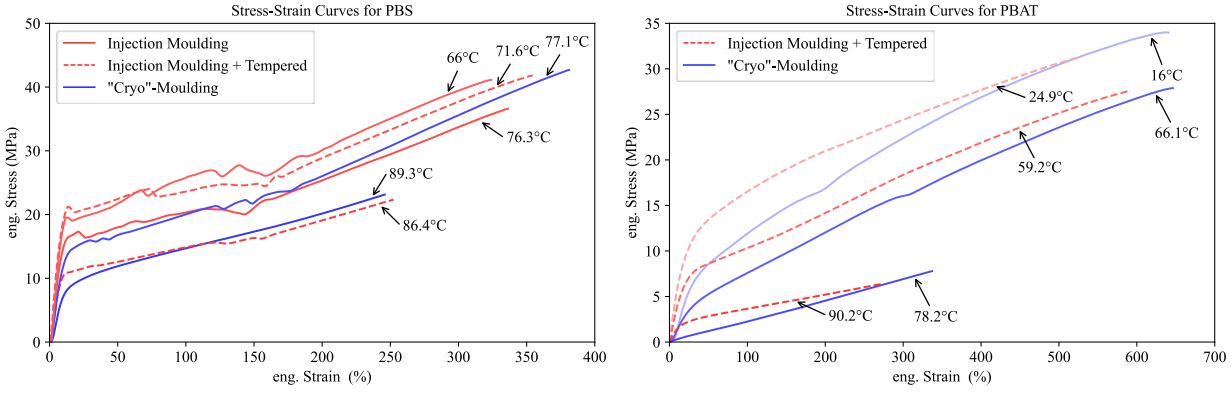

Figure 3. Tensile testing results for PBS (left) and PBAT (right) for selected temperatures and conditions.

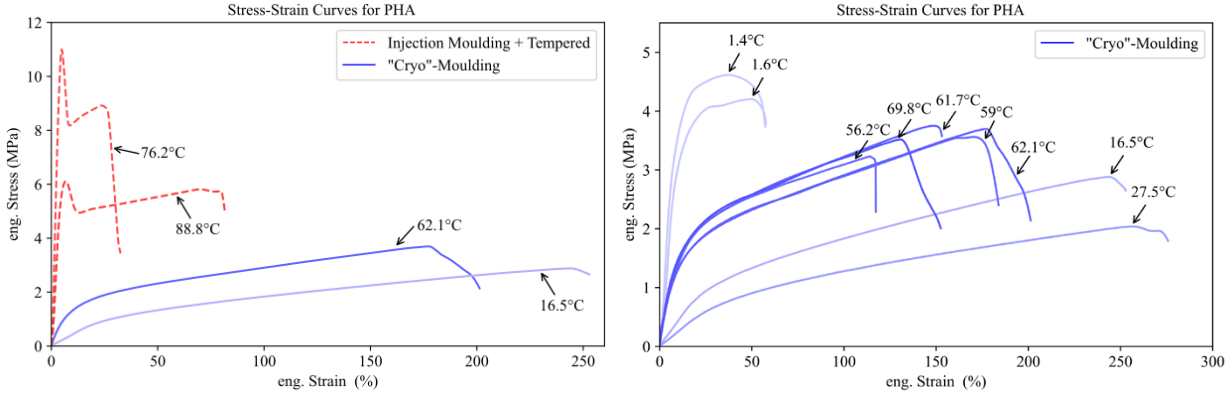

Figure 4. Tensile testing results for PHA. Comparison of the conventional and CIM process (left). Comparing the ductile behavior of the CIM process (right).

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In contrast, the revealed stress-strain behavior of the specimens made of PHA in its amorphous state is significantly different from the known crystalline condition. In Figure 4, the different processes change the material from a brittle and stiff state to a ductile and stretchable material. This leads to a significantly higher elongation at break and lower stresses. In the comparison for the behavior of the ductile material for different temperatures, at low temperatures of approximately 1.5°C the core of the material is assumable still colder than glass transition and behaves stiffer with a strain at break at around 50%. With rising temperatures (16.5°C and 27.5°C) the material softens and the elongation at break is at approximately 250%. From temperatures of approximately 56°C and higher, the material behaves stiffer again and the measured strains at break range from 100% to 200%. This gain in stiffness could be assigned to the thermal induced crystallization that might already occur at these temperatures.

Conclusion

The presented CIM process and tensile testing is capable of revealing the behavior of thermoplastic materials in a highly amorphous state, although they are usually in their semi crystalline state, when processed and handled conventionally. A method with its thermal processing history is presented and mechanical material properties are compared. Particularly for PHA, the mainly amorphous state is difficult to achieve and the characterization of the stress-strain behavior for this state is unobserved. With the presented process, strains of more than 250% have been observed for PHA. These strains are multiple times higher compared to those achieved with the same material in its crystallized state, demonstrating a ductile material behavior. This observed material behavior could be advantageous to produce formed containers.

Alongside this finding, a significant improvement of the molding process for biopolymers was found by CIM. Since the specimens are cooled down to temperatures far below their glass transition, they are stiff and therefore they can be unmolded fast and easily.

The study demonstrates how biopolymers, especially PHA, become more deformable under amorphous conditions. Besides rapid cooling and keeping the material below Tg, there are other methods to avoid big spherulitic crystals, such as using nucleation additives to change the material structure or forming it from the melt, for example, as done in the one-stage injection stretch blow molding process.

Acknowledgments

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