



Institute of Condensed Matter
and Nanosciences

3D-Printed Hierarchically-Porous Objects from the Control of Phase Separation in Semicrystalline PLA/PEG Blends

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Abstract

This thesis presents a solvent-free strategy for fabricating hierarchically porous biomaterials based on poly(L-lactic acid) (PLA) and polyethylene glycol (PEG). The approach exploits crystallization-induced phase separation in PLA/PEG blends, followed by PEG extraction, to generate tunable microporosity and multi-scale porous architectures. The influence of PEG content and molar mass on the crystallization kinetics, spherulitic morphology, and phase distribution of PLA/PEG blends was systematically investigated using differential scanning calorimetry (DSC and flash DSC), polarized optical microscopy (POM) and X-ray diffraction (XRD). An experimental phase diagram of the PLA/PEG system was constructed using flash DSC, based on the distinct thermal transitions observed across different blend compositions and isothermal temperatures. This diagram enabled the prediction of PEG localization and the resulting microporosity ($<50\text{ }\mu\text{m}$) after selective extraction, which, combined with macroporosity introduced through fused deposition modeling (FDM), resulted in a hierarchical porous architecture. Micro-computed tomography (μCT) and scanning electron microscopy (SEM) confirmed the presence of a continuous microporous network across both cast films and 3D-printed structures. Mechanical testing revealed that macroporosity significantly reduced performance, whereas microporosity had a lesser impact, as residual PEG, after extraction, preserved flexibility. Crystallization-driven phase separation provides a versatile strategy to tailor the morphology and mechanical properties of hierarchically porous systems. This approach demonstrates the fabrication of porous structures with complex geometries using readily available materials and solvent-free processing methods. Such a strategy enables on-site production of patient-specific implants and may significantly accelerate treatment timelines in the context of personalized medicine.

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List of symbols

δ	Impurity-rich layer thickness at the interface of growing spherulite
μCT	Micro-computed tomography
CNT	Classical nucleation theory
D	Diffusion coefficient of impurities in the melt
DSC	Differential scanning calorimetry
ECM	Extracellular matrix
FDM	Fused deposition modeling
fDSC	Flash differential scanning calorimetry
FFF	Fused filament fabrication
G	Spherulitic growth rate
iPS	Isotactic polystyrene
k	Boltzmann constant
LL	Liquid-liquid (phase separation)
LS	Liquid-solid (phase separation)
M_n	Number-average molar mass
M_w	Weight-average molar mass
NMR	Nuclear magnetic resonance

| List of symbols

PBAT	_____	Poly(butylene adipate-co-terephthalate)
PCL	_____	Polycaprolactone
PDLA	_____	Poly(D-lactic acid)
PEG	_____	Poly(ethylene glycol)
PESU	_____	Poly(ethylene succinate)
PHB	_____	Polyhydroxybutyrate
PLA	_____	Poly(lactic acid)
PLGA	_____	Poly(lactic-co-glycolic acid)
PLLA	_____	Poly(L-lactic acid)
POM	_____	Polarized optical microscopy
PVDF	_____	Poly(vinylidene fluoride)
SEM	_____	Scanning electron microscopy
SLA	_____	Strereolithography
SLS	_____	Selective laser sintering
T_c	_____	Crystallization temperature
T_g	_____	Glass transition temperature
T_m	_____	Melting temperature
$t_{c1/2}$	_____	Half time of crystallization
T_{cc}	_____	Cold crystallization temperature
T_{hold}	_____	Isothermal holding temperature
TIPS	_____	Thermally induced phase separation
T_m°	_____	Equilibrium melting temperature
UV	_____	Ultraviolet
XRD	_____	X-ray diffraction

PART I

State of the Art

1

Context of the research

Porous materials with hierarchical architectures are widely encountered in natural systems, such as wood, sponges or coral reefs and in biological tissues, including bone and lung. Their structural organization combines pores of varying sizes and geometries, arranged across multiple length scales, to achieve functional efficiency. Mimicking such complexity in synthetic systems remains a considerable challenge due to the difficulty of controlling both the spatial distribution and interconnectivity of pores at different scales [1, 2, 3]. Nevertheless, the significance of such architectures lies in their ability to facilitate effective mass transport, increase surface-to-volume ratio and support gradients of mechanical or biochemical signals, thereby making them particularly attractive for applications in tissue engineering, catalysis and filtration.

Designing materials capable of interacting appropriately with the human body remains a central challenge in biomedical engineering. To meet this challenge, the integration of attributes such as biocompatibility, biodegradability, mechanical properties and adaptability to physiological conditions is essential. Among the various material strategies, the introduction of controlled porosity into polymeric systems has emerged as a key approach to tailor both physical and biological performance. In particular, hierarchical porous structures, combining micro- and macro-porosity, have shown great potential in mimicking the structural complexity of native tissues,

thereby promoting essential functions such as nutrient transport, cellular colonization and vascular integration [4, 5]. Figure 1.1 illustrates the different length scales involved in a porous scaffold and highlights how each level of porosity contributes to the material's functional performance, including its mechanical behavior, permeability and ability to support tissue regeneration.

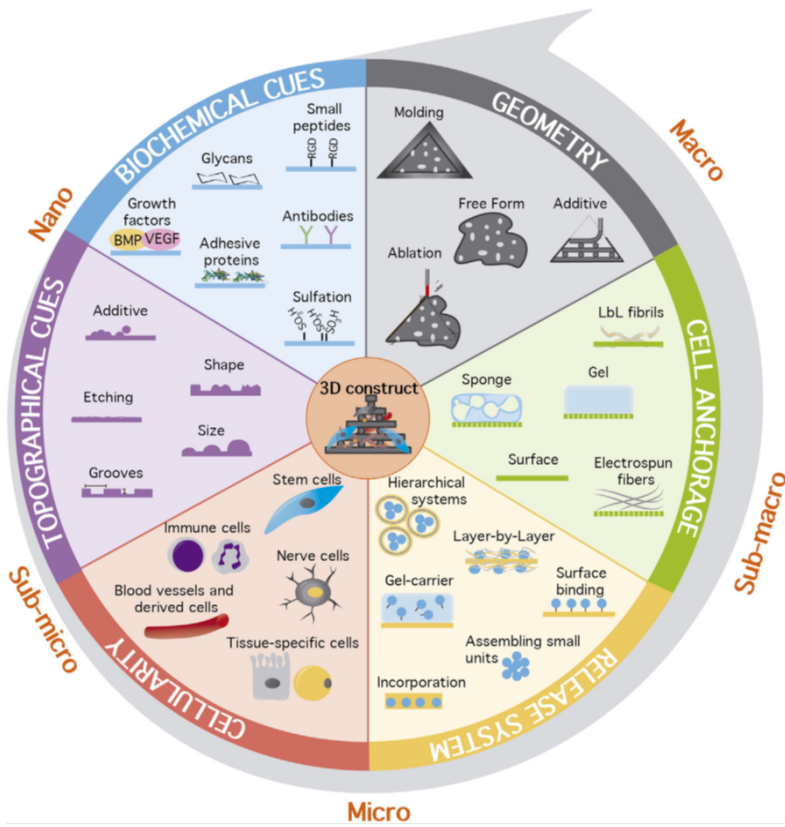


Fig. 1.1 Hierarchy of scaffold porosity and its impact on structural and biological functions. The different porosity scales correspond to macro (>10 mm), sub-macro ($100\ \mu\text{m}$ – 10 mm), micro ($1\ \mu\text{m}$ – $100\ \mu\text{m}$), sub-micro ($100\ \text{nm}$ – $1\ \mu\text{m}$) and nano ($<100\ \text{nm}$) [6].

Porous materials are characterized by interconnected void networks whose dimensions, morphology and distribution determine critical prop-

erties. On the microscopic scale, porosity enhances diffusional transport, which is essential for nutrient delivery, metabolic waste removal and localized release of bioactive agents in tissue engineering constructs [2]. On the macroscopic level, porosity plays a decisive role in determining mechanical characteristics such as stiffness, toughness and deformation response. Beyond individual effects, hierarchical porosity enables the coupling of distinct physical regimes, to ensure mass transport and mechanical function.

The functional importance of multiscale porosity has been extensively illustrated by Oliveira et al. [6], who proposed a framework for categorizing scaffold properties according to both their biological roles and characteristic length scales. In their analysis, summarized in Figure 1.1 of their review, macro-porosity (typically $>100\text{ }\mu\text{m}$) defines the overall geometry and mechanical compliance of the structure, while micro- and sub-microporosity ($1\text{--}100\text{ }\mu\text{m}$ and below) control cell attachment, tissue ingrowth and local biochemical signaling. This hierarchical integration allows spatial and temporal coordination of biological processes within a single construct.

Biodegradable polymers, both natural and synthetic, offer considerable advantages in regenerative medicine by eliminating the need for secondary surgery and by enabling controlled degradation kinetics synchronized with tissue healing. Among them, aliphatic polyesters and polyethers such as polylactic acid (PLA), polycaprolactone (PCL), polyethylene glycol (PEG) and their copolymers have been widely adopted due to their predictable degradation behavior, mechanical versatility and favorable host response profiles. As emphasized by Ulery et al. [7], key parameters such as polymer crystallinity, molar mass and hydrophilicity govern both the resorption kinetics and the biological performance of these materials. Recent studies by Zeinali et al. [8] have further demonstrated that when processed via thermally induced phase separation (TIPS), such polymers can yield scaffolds with high porosity and tunable architecture, while preserving biocompatibility. Furthermore, PLA- and PCL-based materials have been shown to be compatible with a wide range of 3D printing techniques, allowing the fabrication of scaffolds with hierarchical architectures that meet the structural and biological demands of tissue-specific applications [9, 10].

In the context of personalized medicine, the capacity to design and produce anatomically customized systems represents a major advancement in regenerative therapies. As demonstrated by Maintz et al. [11], the on-site 3D printing of bioresorbable implants at the hospital enables the rapid fabrication of patient-specific devices directly from medical imaging data,

significantly reducing the time between diagnosis and intervention. This point-of-care approach allows for precise control over scaffold geometry, porosity and degradation behavior, aligning the implant's characteristics with the physiological and anatomical requirements of the individual.

Despite their potential, hierarchical porous structures remain difficult to fabricate in a controlled and reproducible manner. Conventional techniques offer limited control over the multiscale organization of pores [2]. Recent strategies combining phase separation mechanisms with additive manufacturing have opened promising avenues to address this limitation [8, 12]. In these hybrid approaches, parameters such as thermal history, crystallization kinetics and polymer compatibility are exploited to guide phase separation and subsequent pore formation. This permits the fabrication of biodegradable constructs with tunable and spatially resolved porosity, optimized for targeted biological functions [13].

Overview of the Research Approach

To better understand the structure of the present literature review, it is important to briefly outline the scientific motivations behind this thesis. The research aims to develop a strategy for fabricating polymeric materials with controlled hierarchical porosity, using only abundant, biocompatible components and solvent-free processing routes. In this approach, PLA is combined with PEG, which serves both as a porogen and as a plasticizer. Phase separation between PLA and PEG is induced by PLA crystallization under controlled thermal conditions, allowing subsequent PEG extraction in water to generate microporosity. This method is coupled with 3D printing of PLA/PEG blends prior to PEG removal, enabling the simultaneous creation of macroporosity. The resulting dual-porous structures exploit the complementary advantages of additive manufacturing and thermally driven phase separation, without requiring toxic solvents or complex processing steps. This low-cost and scalable approach is particularly suited to the development of customizable implants tailored to patient-specific clinical needs. These objectives form the conceptual backbone of the following state-of-the-art, which has been structured to progressively examine the individual scientific challenges related to material selection, phase behavior, crystallization, and porosity control in PLA/PEG systems.

2

Principles of polymer crystallization

Semicrystalline polymer crystallization is a semi-ordering process in which polymer chains, initially in a disordered molten or solution state, organize into lamellar structures upon cooling or solvent evaporation. To exhibit crystallinity, the polymer chains must possess sufficient regularity and chain symmetry to allow local packing into ordered lamellae. Unlike small molecules, polymers rarely form large single crystals. Instead, they crystallize into semicrystalline morphologies called spherulites, which consist of a radial arrangement of crystalline lamellae alternating with amorphous regions where the chains remain disordered and entangled. As illustrated schematically in Figure 2.1, a spherulite originates from a central nucleation point and expands through the radial propagation of crystalline lamellae. These lamellae, which consist of folded polymer chains, are separated by amorphous regions, forming a hierarchical structure with alternating ordered and disordered domains.

These structures emerge when crystallization occurs from a melt under conditions of large undercooling ΔT , the difference between the melting temperature (T_m) and the crystallization temperature (T_c) [14]. Undercooling enhances the thermodynamic driving force for crystallization and accelerates the nucleation and growth process. For polymers, crystallization occurs

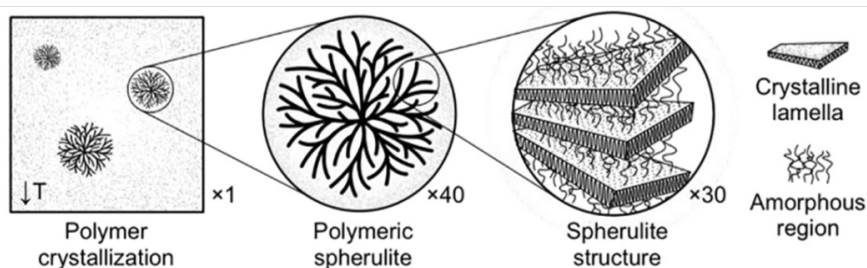


Fig. 2.1 Schematic structure of polymer spherulites at different magnification level, adapted from [5].

mostly from viscous liquids, a condition which restricts molecular diffusion and facilitates the establishment of sharp growth fronts [15].

The resulting spherulitic morphology imparts specific optical and mechanical characteristics to semicrystalline polymers. At the macroscopic level, birefringent patterns are observed due to radial lamellar organization, while at the nanoscopic scale, alternating lamellae and amorphous domains provide a balance between rigidity and flexibility. This hierarchical organization defines the overall performance of semicrystalline materials.

2.1 Mechanism of crystal nucleation and growth

Nucleation is the initial step in the crystallization of polymers and governs both the number and spatial distribution of spherulites appearing within the amorphous matrix. Two distinct but interrelated nucleation processes are generally distinguished: primary nucleation, which determines the density of spherulites and secondary nucleation, which controls the rate and mode of lamellar growth. In polymer systems, crystallization is predominantly governed by kinetic factors rather than thermodynamic equilibrium, due to constraints arising from high molar mass, chain entanglement and limited segmental mobility. In this context, several theoretical models have been proposed to describe polymer crystallization. Among them, the framework developed by Hoffman and Lauritzen [16], which explains nucleation and growth from bulk melts through the formation of folded-chain lamellae with lamellar growth being controlled by a free energy barrier of secondary nucleation, remains the most widely accepted. However, models based on

entropic barriers are gaining popularity.

2.1.1 Primary nucleation : Origin of spherulites

Primary nucleation marks the beginning of the crystallization process, where a critical nucleus forms either spontaneously or at an interface within the supercooled melt. The primary nucleation can be either homogeneous, which occurs in the absence of foreign surfaces or heterogeneous, which relies on interfaces to reduce the energy barrier to nucleus formation.

Homogeneous nucleation Homogeneous nucleation is rare in polymer systems due to the high free energy required to stabilize a critical nucleus in a melt of entangled polymer chains. Theoretical estimates show that this pathway becomes feasible only under extreme undercooling [17]. Consequently, homogeneous nucleation is mostly limited to ideal, ultrapure or strongly divided systems and, in practice, plays a minor role in practical crystallization.

Heterogeneous nucleation Heterogeneous nucleation is the dominant mechanism in bulk polymer crystallization. It occurs at interfaces such as impurities or container surfaces, which reduce the interfacial free energy required to stabilize the crystalline embryo. The term impurities refer to any species distinct from the crystallizing polymer, including dust particles, nucleating agents specifically added to promote crystallization or secondary polymer phases in blends, such as droplets or chains of a different polymer. Heterogeneous nucleation can also occur through self-seeding, where highly stable crystalline fragments of the same polymer are intentionally formed to act as nucleation sites [18].

The nucleation rate is exponentially dependent on the degree of undercooling ($\Delta T = T_m - T_c$) and the interfacial energy (σ). According to classical nucleation theory (CNT), the nucleation rate (J) is given by [19]:

$$J \propto \exp\left(-\frac{\Delta G^*}{kT}\right), \quad \text{with} \quad \Delta G^* \propto \frac{\sigma^3}{(\Delta T)^2} \quad (2.1)$$

and k the Boltzmann constant

Therefore, the number of spherulites is governed by the number of nucleation sites, which increases strongly with decreasing crystallization temperature, then decreases when going further downward T_g . This behavior arises from the interplay between an increasing thermodynamic driving force, which promotes nucleation as the degree of undercooling increases and a simultaneous reduction in chain mobility at lower crystallization temperatures, which kinetically hinders the necessary molecular rearrangements.

2.1.2 Secondary Nucleation: Mechanism of Lamellar Growth

Secondary nucleation governs the formation of new crystalline chain segments at the interface between the melt and a growing lamella. This process does not create new spherulitic entities but instead enables the continuous extension of pre-existing lamellae, leading to the radial expansion of spherulites. It is a local event restricted to the growth front and is essential to the propagation of folded-chain lamellae in polymer crystallization. Energetically, primary nucleation involves the formation of a new ordered domain from the disordered melt, typically requiring a high free energy input. In contrast, secondary nucleation occurs on an existing crystalline substrate, substantially lowering the energy barrier for the formation of new crystalline segments. Spatially, primary nucleation defines the distribution of spherulites in the bulk, whereas secondary nucleation is confined to the nanoscale vicinity of the crystal–melt interface and determines the kinetics of lamellar propagation.

In the theoretical framework established by Hoffman and Lauritzen [16], secondary nucleation is treated as a rate-determining step that involves the formation of a surface nucleus on the lateral face of a lamellae. The linear growth rate (G) of lamellae is given by:

$$G = G_0 \exp \left(-\frac{U^*}{R(T - T_\infty)} \right) \exp \left(-\frac{K_g}{fT\Delta T} \right) \quad (2.2)$$

where G_0 is a pre-exponential factor, U^* is the activation energy for the diffusive transport of chain segments to the growth front, R is the gas constant, T_∞ is the hypothetical temperature at which mobility ceases (commonly 30-50K below T_g), K_g is the nucleation constant related to the free energy cost of forming a new crystalline surface and f is a correction factor. In

other words, the first exponential reflects the mobility-limited transport of chains and the second accounts for the thermodynamic barrier to nucleation.

A critical feature of this equation is the non-monotonic dependence of G on crystallization temperature T_c that typically follows a bell-shaped curve, as nucleation is thermodynamically limited near T_m and kinetically hindered near T_g , due to insufficient chain mobility.

Experimentally, this maximum can be identified using polarized optical microscopy by tracking the spherulite radial growth rate or through isothermal differential scanning calorimetry (DSC) by measuring the crystallization kinetics as a function of temperature. The temperature at which G is maximized provides insight into the balance between nucleation efficiency and chain mobility and depends on polymer characteristics such as molar mass and segmental flexibility.

2.2 Controlling Parameters

Several experimental variables affect nucleation processes and influence both the rate and morphology of polymer crystallization.

Undercooling (ΔT), as briefly explained previously, controls the thermodynamic driving force for crystallization. At high T_c , near the melting point T_m , the thermodynamic driving force is small and nucleation is energetically unfavorable. Conversely, at low T_c , near the glass transition temperature, chain mobility is severely restricted, impeding the molecular rearrangements required for crystallization. As a result, the growth rate G exhibits a maximum at an intermediate temperature and decreases toward zero at both extremes, forming a bell-shaped curve characteristic of polymer crystallization kinetics, as presented in Figure 2.2. This behavior reflects the competing influences of thermodynamics and molecular mobility.

Molar mass exerts a complex influence on nucleation behavior. High molar mass polymers exhibit slower crystallization kinetics due to reduced chain mobility and longer relaxation times. This hinders both the formation of stable nuclei and the propagation of lamellae, particularly at low undercooling where the thermodynamic driving force is moderate. This behaviour can be observed in Figure 2.2, that shows the temperature dependence of the linear crystal growth rate as a function of molar mass for

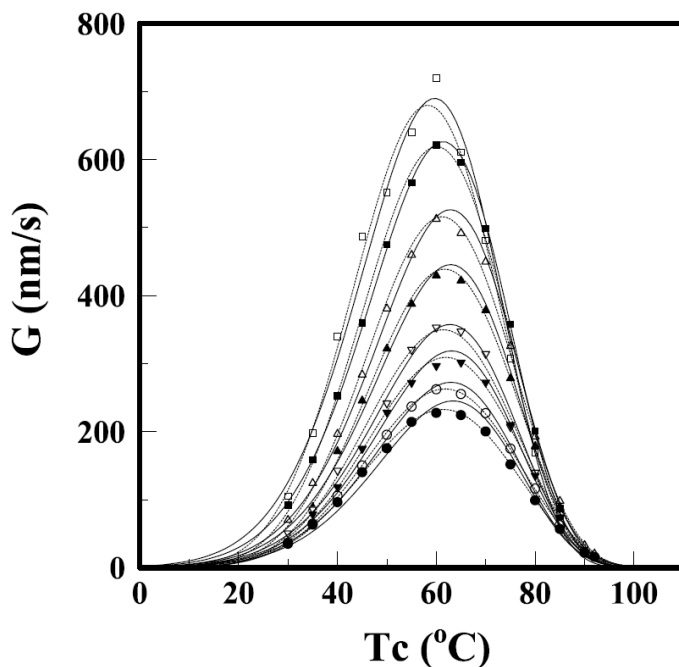


Fig. 2.2 Temperature dependence of spherulite growth rate (G) of Poly(ethylene succinate) depending on molar mass. Symbols are for molar masses ranging from 3.5 kDa ($\square$) to 21.2 kDa ($\bullet$). Solid lines are fits to Eq. 2.2 taken from [20].

Poly(ethylene succinate) (PESU) ranging from 3.5 to 21.2 kDa [20].

Melt viscosity is a nearly universal prerequisite for spherulitic growth in polymers. High viscosity suppresses long-range diffusion, which stabilizes the growing front and facilitates the formation of organized lamellae. Typically, spherulitic growth emerges from viscous melts, where chain segments are mobile enough to fold and crystallize locally but restricted enough to maintain a well-defined growth interface [14]. Excessively low viscosity, by contrast, tends to destabilize the front and disrupt ordered growth.

Nucleating agents serve as heterogeneous nucleation sites and modify the energy landscape at the interface between the melt and the forming crystal. Their effectiveness depends on chemical compatibility, surface energy and crystallographic matching with the polymer matrix. By lowering the

nucleation barrier, these additives can significantly increase the number of nucleation events, leading to finer spherulitic textures and shorter induction times during crystallization.

Cooling rate determines the time available for nucleation and growth during non-isothermal processing. Rapid cooling increases the nucleation rate by rapidly achieving the required undercooling, resulting in a higher density of smaller spherulites. However, it simultaneously limits the time for lamellar growth and thickening and can lead to incomplete crystallization. Conversely, slower cooling allows for more extensive crystal growth but may favor coarser morphologies with fewer nucleation events [21].

Ultimately, the crystallization behavior of polymers results from a complex interplay between kinetic and thermodynamic factors. This interplay can be modulated through processing parameters, allowing for both the control of crystallization kinetics and the regulation of the resulting crystalline microstructure.

2.3 Special crystalline structures of polymers

2.3.1 Polymorphism

While the previous sections focused on the formation and growth of lamellae and spherulites, it is important to note that under certain conditions, a given polymer may crystallize into structurally distinct forms. This phenomenon, known as polymorphism, refers to the ability of a single polymer to adopt multiple crystalline arrangements depending on factors such as temperature, molecular architecture or processing history. These polymorphic forms may differ in chain conformation, unit cell symmetry or chain packing density and often exhibit different thermodynamic stabilities. Crystallization temperature is a primary determinant of polymorphic selection: lower temperatures tend to favor kinetically accessible but less stable forms, while higher temperatures allow for more thermodynamically favorable arrangements. The chemical structure of the polymer also plays a central role, particularly through factors such as chain stiffness, tacticity and stereoregularity, which influence how chains can fold or align during nucleation and growth. Additionally, thermal history, including melt–recrystallization

cycles, cooling rate or annealing, can shift the balance between competing polymorphs by altering chain mobility or seeding specific crystalline domains [14, 22].

Beyond temperature and thermal protocol, mechanical deformation during crystallization has also been shown to promote the formation of specific polymorphs. Crystallization under stress or shear flow can induce molecular orientation and favor mesophases or metastable polymorphs distinct from those observed under quiescent conditions. Such orientation-driven polymorphism is especially relevant in processing contexts like fiber spinning or injection molding, where flow-induced crystallization often leads to highly anisotropic crystalline textures [23].

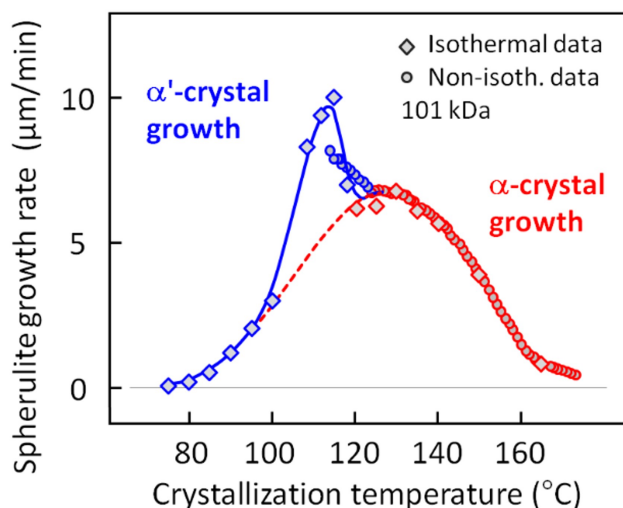


Fig. 2.3 Temperature dependence of spherulite growth rate (G) of PLLA showing different crystal types, α' (in blue) and α (in red) for isothermal (squares) and non-isothermal conditions (circles). Adapted from [24].

Polymorphism can also influence the spherulitic growth rate. In the case of PLA, for example, the coexistence of multiple crystalline forms depending on the thermal history may lead to a bimodal temperature dependence, rather than the typical single bell-shaped profile (as seen on Figure 2.3. This behavior arises from the coexistence of two distinct crystallization regimes:

the α' form predominates at lower crystallization temperatures, while the α form becomes dominant at higher temperatures. These regimes reflect not only differences in thermodynamic stability and chain mobility but may also involve distinct nucleation mechanisms [24]. Although direct evidence remains limited, current understanding suggests that the less ordered α' polymorph can form via homogeneous nucleation, particularly under conditions of low temperature or reduced impurity content, where few heterogeneous sites are available. In contrast, the more stable α phase is typically associated with heterogeneous nucleation, promoted by interfaces, impurities, or specific nucleating agents that lower the energy barrier for crystallization and facilitate faster spherulitic development.

2.3.2 Banded spherulites

Beyond the overall radial growth of spherulites, certain polymers develop periodic optical features known as banded spherulites. These structures are characterized by concentric rings visible under polarized light, as shown in Figure 2.4. The formation of such banded patterns suggests that, under specific conditions, lamellae do not grow strictly radially but instead adopt a twisted or helicoidal trajectory [25].

The emergence of banded spherulites has been widely attributed to the periodic twisting of lamellae during radial growth, which induces a periodic modulation of the optical orientation of the axes observable under cross-polarized light [26]. This twisting behavior is particularly prominent in chiral polymers where the helical nature of the polymer chain is believed to drive coherent lamellar rotation. In these systems, banding typically appears over broad crystallization temperature ranges and exhibits regular spacing that correlates with temperature, molar mass and crystallization kinetics.

In addition to chirality, banded morphologies can also appear in polymer blends, where phase separation, differential crystallization rates or interfacial constraints can perturb the lamellar growth front. When one component crystallizes within a phase-separated matrix, the confinement or mechanical stress at the interface may induce or disrupt lamellar twisting. The resulting morphologies can include irregular or asymmetric banded spherulites, depending on the miscibility and crystallization sequence of the blend

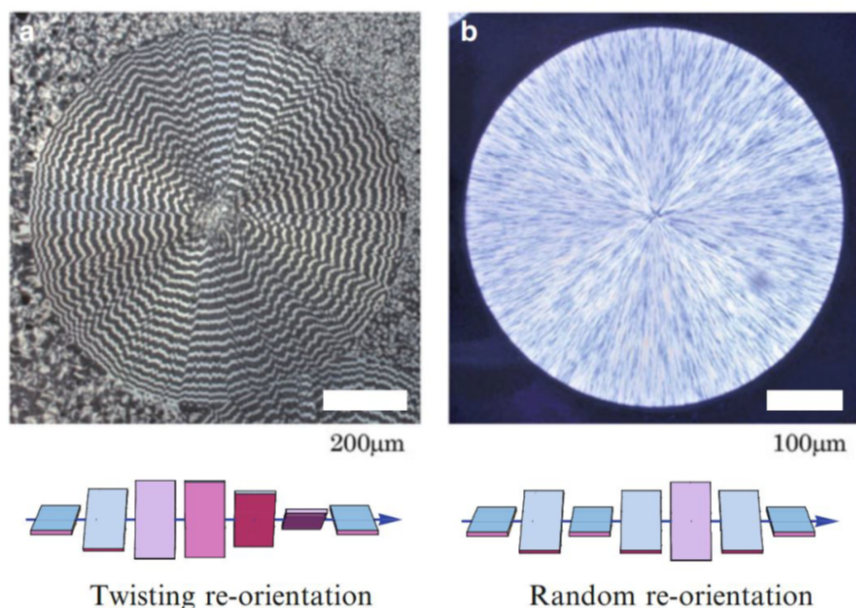


Fig. 2.4 Comparison between banded and non-banded spherulites made of poly(vinylidene fluoride) (PVDF) (a) and isotactic polystyrene (iPS) (b) observed by POM, taken from [25].

components. In these multicomponent systems, the formation of banded spherulites has been shown to depend more sensitively on the degree of supercooling than on the absolute crystallization temperature [27], suggesting that the thermodynamic driving force plays a critical role in determining the onset and regularity of band formation under non-equilibrium conditions.

2.4 Biocompatible polymers

Biomaterials are engineered substances designed to interact with biological systems for therapeutic or diagnostic purposes. In the context of regenerative medicine and tissue engineering, biomaterials serve as structural and functional scaffolds that can support cellular activities, guide tissue regeneration and deliver bioactive molecules in a controlled manner. Among the wide range of materials investigated for these purposes, natural and

synthetic polymers have emerged as particularly promising due to their respective advantages: natural polymers are generally biocompatible and biologically active, whereas synthetic polymers offer greater tunability in terms of structure, degradation behavior and processability.

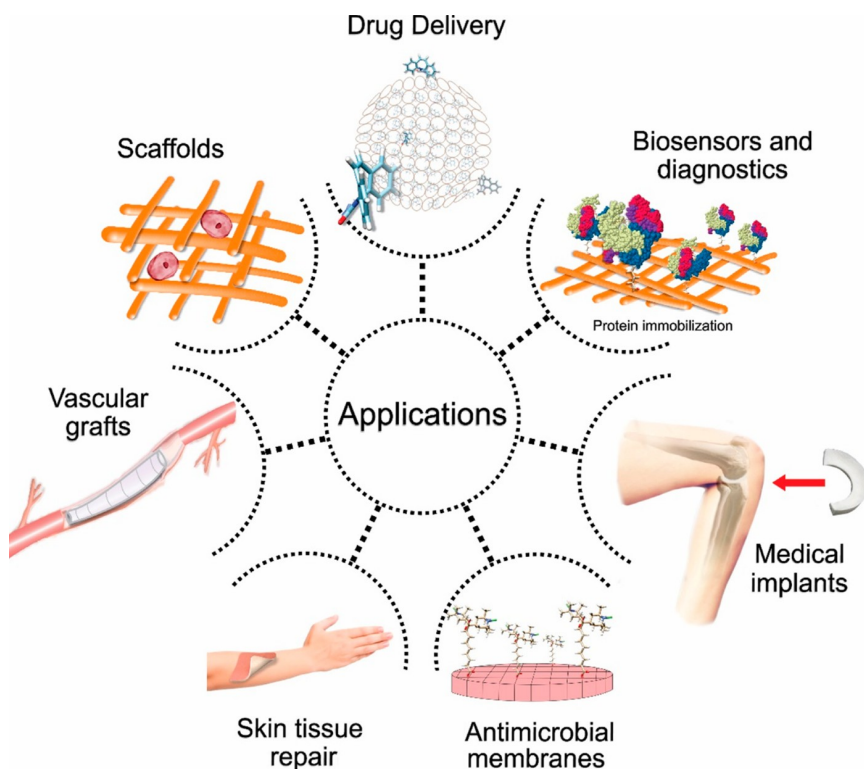


Fig. 2.5 Overview of biomedical applications using biocompatible polymers, taken from [28].

Over the past two decades, the scope of polymer use in biomedical applications has expanded considerably, as illustrated by the diversity of roles depicted in Figure 2.5. As emphasized by Premkumar et al., polymers are no longer viewed merely as passive scaffolding materials, but as active participants in the therapeutic process. Stimuli-responsive or "smart" polymers, capable of reacting to changes in temperature, pH, or biochemical signals, have enabled the design of dynamic systems for drug delivery and tissue regeneration. Furthermore, the integration of polymers into advanced fab-

rication technologies, such as 3D printing has made it possible to produce complex, hierarchical structures that better mimic the architecture of native tissues and can be tailored to individual patients. In this evolving landscape, the choice of a polymer is increasingly governed not by a universal material standard but by the specific biological, mechanical and degradation criteria required for each application context [28].

2.4.1 Natural polymers

Natural polymers represent a class of materials that are inherently biocompatible and well-suited to interact with biological systems. Their structural and biochemical similarity to components of the extracellular matrix (ECM) renders them ideal for promoting cellular adhesion, proliferation and tissue integration. Among the most widely studied are collagen, fibrin, chitosan, alginate and hyaluronic acid. Collagen, in particular, is extensively used due to its presence in connective tissues and its ability to support cell anchorage and matrix deposition [29].

However, despite their favorable biological properties, natural polymers suffer from several limitations. One major drawback is their uncontrolled degradation profile, which may lead to premature loss of mechanical integrity or structural support during tissue regeneration. In addition, their mechanical properties are typically poor, making them unsuitable for load-bearing applications without further reinforcement. Another challenge is their susceptibility to microbial contamination and batch variability, which complicates large-scale synthesis and regulatory approval. Moreover, because these polymers are often derived from animal or human tissues, they can induce immune responses or allergic reactions in certain individuals [30].

To overcome these drawbacks, current strategies involve combining natural polymers with synthetic ones to create composite materials with improved mechanical and degradation properties while retaining biocompatibility. These hybrid systems are increasingly explored for wound dressings [31], hydrogels and scaffolds for soft tissue regeneration [32].

2.4.2 Synthetic polymers

Synthetic polymers have become essential in the design of biomedical devices and tissue engineering scaffolds due to their tunable physico-chemical properties, structural stability and scalability in manufacturing. Compared to natural polymers, they offer greater reproducibility and mechanical robustness, allowing for precise control over architecture and degradation rates.

Among the most studied synthetic polymers are polylactic acid (PLA), polycaprolactone (PCL) and poly(lactic-co-glycolic acid) (PLGA). These materials are FDA-approved for various biomedical applications and have demonstrated excellent biocompatibility and degradability into non-toxic byproducts. One of the critical advantages of synthetic polymers is their customizable degradation behavior. By adjusting parameters such as molar mass, crystallinity and copolymer composition, the rate of hydrolytic degradation can be tailored to match the timeframes required for tissue healing or drug delivery. For instance, PLGA copolymers can be tuned by varying the lactic-to-glycolic acid ratio, thereby achieving degradation rates ranging from weeks to months [33].

Mechanical properties are another important consideration in scaffold design. Synthetic polymers offer a wide range of tensile strength, elasticity and toughness. PCL, for example, is particularly attractive for applications requiring long-term mechanical support due to its high elongation at break and slow degradation rate. On the other hand, PLA is more brittle but offers higher strength and stiffness, which may be desirable in certain orthopedic or dental applications [34].

These polymers can be processed into various shapes, such as porous sponges, electrospun mats, injectable hydrogels and 3D-printed constructs [30]. Each configuration presents distinct advantages in terms of mechanical performance, degradation profile, and interaction with the biological environment. The structural design of the scaffold, particularly its dimensional architecture and connectivity, modulates cell adhesion and nutrient exchange. These factors collectively influence the biological response to the material and need to be taken into considerations in the development of effective biomaterial scaffolds for regenerative applications [35].

Advanced manufacturing techniques, particularly extrusion-based 3D

printing such as fused deposition modeling (FDM), have significantly expanded the functional utility of synthetic polymers in biomedical applications. Thermoplastic polymers like polylactic acid (PLA) and polycaprolactone (PCL) are particularly well suited to FDM due to their favorable melting behavior, mechanical stability, and biodegradability. These materials can be processed into patient-specific constructs with tailored porosity and internal architecture, enabling a broad range of clinical uses, including drug delivery systems, surgical instruments and tissue engineering scaffolds, as illustrated in Figure 2.6. However, the mechanical robustness of thermoplastic filaments often comes at the cost of limited bioactivity, necessitating surface modification to enhance cell-material interactions. In some applications, polymer blends or composite filaments incorporating bioactive agents are employed to improve functional performance without compromising structural integrity [36].

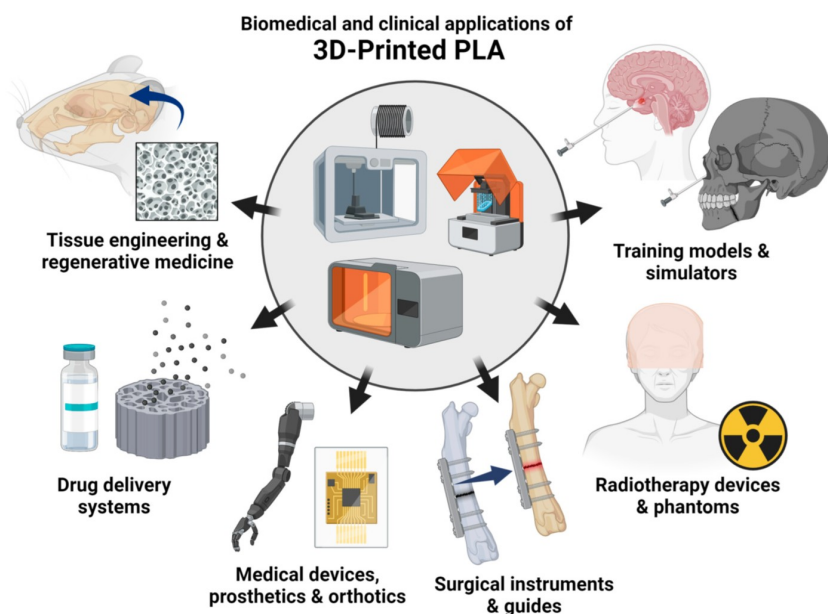


Fig. 2.6 Overview of biomedical and clinical applications of 3D-printed PLA, ranging from tissue engineering and drug delivery to surgical tools and implantable devices, taken from [37].

In contrast to thermoplastic filaments, synthetic polymers can also be

processed as hydrogels with high water content. This leads to larger elasticity and permeability which are more suited properties for soft tissue applications. Although mechanically weaker, hydrogel-based bioinks can be printed in combination with reinforcing agents to improve their structural stability and functional performance [38].

Drug delivery is another domain where synthetic polymers excel. Their ability to encapsulate, protect and release drugs in a controlled manner makes them ideal candidates for localized therapies. Moreover, layered systems and surface coatings can be integrated to further modulate release kinetics and enhance bioactivity. Composites formed by combining synthetic and natural polymers leverage the advantages of both systems, providing improved mechanical properties while maintaining cellular affinity [39]. As such, polymer-based delivery scaffold offer an effective means of coupling structural support with therapeutic functionality in regenerative medicine.

Synthetic polymers constitute an important element in the design of modern biomaterials, owing to their structural adaptability, tunable degradation profiles and mechanical versatility. Their applications range from load-bearing scaffolds and biodegradable stents to stimuli-responsive drug delivery systems and advanced 3D printed implants. However, despite this versatility, they present certain limitations. Most lack inherent bioactivity, often requiring surface functionalization or blending with biologically derived components to enhance their biological performance. These considerations highlight the need for careful material selection and design optimization in the development of effective polymer-based biomedical scaffolds [30].

2.4.3 Block copolymers

Block copolymers represent a distinct class of macromolecules composed of chemically dissimilar polymer segments covalently linked within a single chain. Their architecture allows finely tuned interactions with the biological environment. In particular, amphiphilic systems that combine hydrophilic blocks such as PEG with biodegradable polyesters like PLA, PLGA or PCL, have shown considerable versatility in scaffold fabrication, where the need for both mechanical support and biocompatibility is paramount [40, 41].

What sets block copolymers apart from conventional polymer blends is their intrinsic structural cohesion at the molecular scale. Rather than relying on mere miscibility, these materials offer a stable phase organization that resists macroscopic separation during processing or degradation. This confers a high level of morphological control during scaffold fabrication and results in more predictable mechanical responses under physiological conditions. For instance, the inclusion of PEG blocks can enhance the elasticity and hydration of otherwise brittle polyesters, yielding scaffolds that better accommodate cellular colonization and remodeling without compromising structural stability [42].

Beyond mechanical and morphological tuning, block copolymers also introduce new possibilities for dynamic functionality. Their ability to self-assemble into nanostructures—micelles, vesicles, or hydrogels—enables the creation of scaffolds that not only support tissue regeneration but also participate in it. Such systems can incorporate and release therapeutic agents in a spatially and temporally controlled manner, which is particularly advantageous in healing environments where bioactivity must evolve over time. The responsiveness of certain formulations to temperature or pH further expands their potential in minimally invasive therapies and injectable constructs [40].

However, the promise of block copolymers is tempered by several limitations. Their synthesis often involves complex chemistries that require careful control over reaction conditions and stoichiometry, limiting scalability and reproducibility. A more fundamental constraint arises from the fact that, despite being composed of distinct blocks, the copolymer behaves as a single macromolecular entity during processing. This unified response can be advantageous for homogenizing material properties, but it also limits the possibility of leveraging the unique behavior of each block independently. Although phase-selective porosity has been achieved in certain block copolymer systems, these approaches have largely been restricted to thin films and rely on sophisticated processing methods. For instance, Charlier et al. demonstrated the generation of nano- and micro-porosity in microphase-separated polyimide-based block copolymer films through thermal degradation of a thermally degradable block acting as a sacrificial phase [43]. While effective at the film scale, such strategies require finely tuned thermal treatments to balance depolymerization and matrix stabil-

ity, and the resulting closed-cell morphologies are not readily transferable to bulk scaffold fabrication. This example illustrates how strategies that rely on selective block degradation, while effective in thin films, are highly sensitive to processing parameters and generate closed-cell morphologies that are difficult to adapt to bulk scaffold fabrication. As a result, in the context of three-dimensional scaffolds, porosity in block copolymers must often be introduced using conventional, non-selective methods rather than by exploiting the selective degradation of one block. Achieving phase-selective porosity, for instance by degrading the hydrophilic segment to leave a porous hydrophobic matrix, would require targeted reactions that add complexity to fabrication and could compromise scaffold integrity. From a regulatory perspective, the presence of synthetic linkages and multi-functional domains raises additional concerns regarding long-term safety and metabolic byproducts [41].

Nonetheless, the integrated nature of block copolymers does not prevent their effective use in scaffold design. On the contrary, their well-defined molecular architecture and tailored viscoelastic properties make them particularly well suited to advanced manufacturing processes that demand fine spatial control. Techniques such as unidirectional freeze casting, electrospinning and extrusion-based 3D printing benefit from the rheological consistency and thermal behavior of these materials [44]. In this context, block copolymers serve not only as structurally robust base materials, but also as enablers of design strategies that seek to align scaffold architecture with specific biological and mechanical requirements.

2.5 Properties and crystallization of PLA

Among all the biocompatible polymers presented above, PLA has emerged as one of the most widely used biodegradable polyesters for biomedical applications, mainly due to its abundance, affordability, degradation and mostly thanks to its thermoplastic processability. Derived from renewable resources such as corn starch or sugarcane, PLA exists in several stereoisomeric forms, primarily poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA), which differ in the chirality of their repeating units, as presented in Figure 2.7. Among these, PLLA is the most commonly used form due

to its higher crystallinity and superior mechanical performance. However, commercially available PLLA generally contains a small proportion of D-lactide units, which can influence the material crystallization behavior and mechanical properties by disrupting the regularity of the polymer chains and reducing the degree of crystallinity.

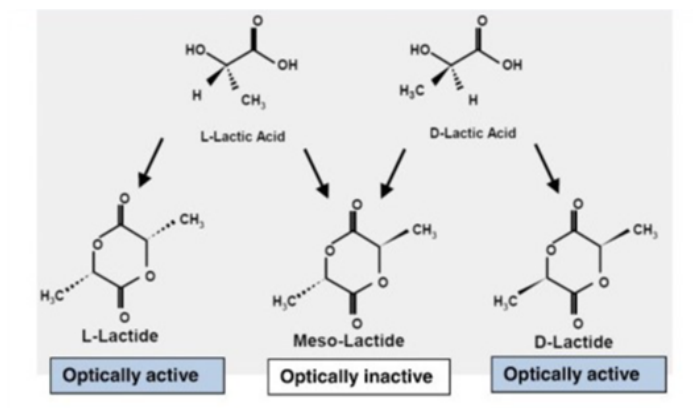


Fig. 2.7 L- and D-enantiomeric forms of lactic acid and their stereoisomers, taken from [45].

PLA degradation by hydrolysis into non-toxic lactic acid, which is metabolized by the body, underpins its favorable biological response and makes it particularly suited for temporary implants and scaffolds in regenerative medicine. In addition to its biodegradability, PLA offers a compelling balance between mechanical strength and tunable degradation rates, which can be tailored by controlling its molar mass and crystallinity. The relatively low processing temperatures of PLA, typically ranging between 180-230 °C, are compatible with a wide range of manufacturing techniques, including extrusion-based 3D printing, thus enabling the design of porous and patient-specific scaffolds.

Although briefly mentioned earlier, it is essential to emphasize that crystallinity plays a central role in determining the most relevant properties of PLA. Indeed, the degree of crystallinity ultimately governs its mechanical performance and biodegradability. The crystalline structure of PLA has a profound impact on both its mechanical behavior and degradation profile. Higher crystallinity typically enhances stiffness and strength, while simul-

taneously reducing the rate of hydrolysis due to reduced water diffusion through the ordered domains. Conversely, amorphous regions degrade faster and offer greater flexibility. This tunability of crystalline content enables the optimization of scaffold properties to meet specific biomedical requirements. As such, understanding and controlling PLA crystallization mechanisms is fundamental to tailor its performance.

2.5.1 Crystalline structures of PLA

Depending on the crystallization conditions, PLA can adopt distinct crystalline forms. The most commonly reported crystalline phases are the α , β , γ , and stereocomplex forms, each characterized by specific chain conformations and unit cell arrangements [46]. The α -form is the most thermodynamically stable and prevalent crystalline phase. It typically forms an orthorhombic unit cell with a 10/3 helical conformation of the polymer chains. A less ordered variant, referred to as α' , is commonly obtained at crystallization temperatures below 120°C and can transform into the α -form upon heating [47]. The β -form, by contrast, is metastable and often generated under specific mechanical stress, leading to a more extended 3/1 helical chain conformation [48]. The γ -form has been rarely observed and is typically induced under particular crystallization conditions, such as epitaxial crystallization on selected substrates [49].

Stereocomplexes can be formed in equimolar mixtures of PLLA and PDLA, giving rise to a distinct co-crystal crystalline phase with significantly enhanced properties. This form is distinguished by a triclinic unit cell and a more tightly packed arrangement due to the complementary interaction of L- and D-chains, resulting in significantly enhanced thermal stability, with melting temperatures approximately 50°C higher than that of the individual homopolymers, as well as improved crystallinity and mechanical performance [50, 51]. Although promising, their use in biomedical applications remains limited by the higher cost and more complex processing requirements associated with enantiomerically pure polymers.

2.5.2 Characteristic temperatures of PLA

The thermal properties of PLA, notably the glass transition temperature (T_g), melting temperature (T_m) and equilibrium melting temperature (T_m°),

are central to understanding its crystallization behavior. The glass transition temperature of PLA typically lies between 55°C and 65°C, depending on molar mass, thermal history and D-lactide content [46]. This dependence is illustrated in Figure 2.8. Below T_g , the polymer is in a rigid, amorphous state with limited chain mobility, while above T_g , increased molecular motion enables segmental rearrangements necessary for crystallization. Therefore, T_g defines the lower limit of thermal processing and determines the mechanical performances, especially the flexibility at the temperature of use.

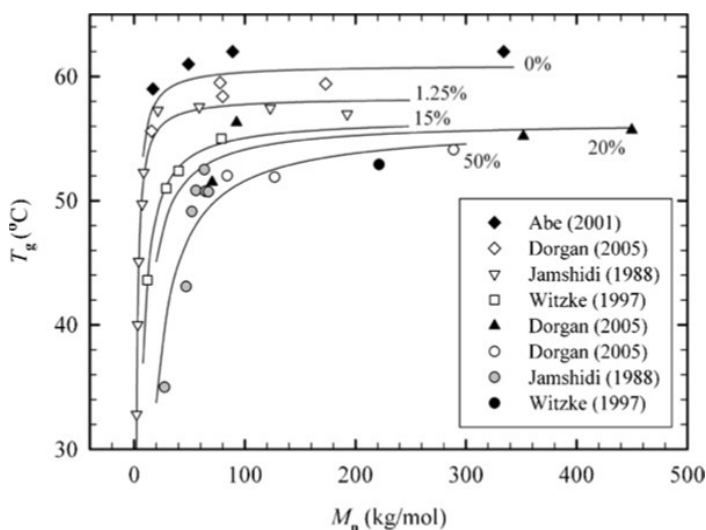


Fig. 2.8 T_g in terms of M_n for different D-lactide contents of PLA, taken from [46].

The melting temperature (T_m) of PLA is dependent on the crystal thickness and is typically observed in the range of 170°C to 180°C. This variations in T_m can result from differences in crystallization conditions or the presence of comonomers. As illustrated in Figure 2.9, both the crystallization temperature (T_c) and the D-lactide (also called minor repeating unit) content influences T_m . At low (T_c), incomplete ordering of chains leads to the formation of less perfect crystals, resulting in reduced T_m . As crystallization temperature increases, lamellar thickness increases and crystalline order improve, thereby increasing T_m . However, this trend is also modulated by the stereochemistry of the chains: an increase in D-content disrupts the stereoregularity required for efficient chain packing, thus decreasing T_m .

even at favorable crystallization temperatures.

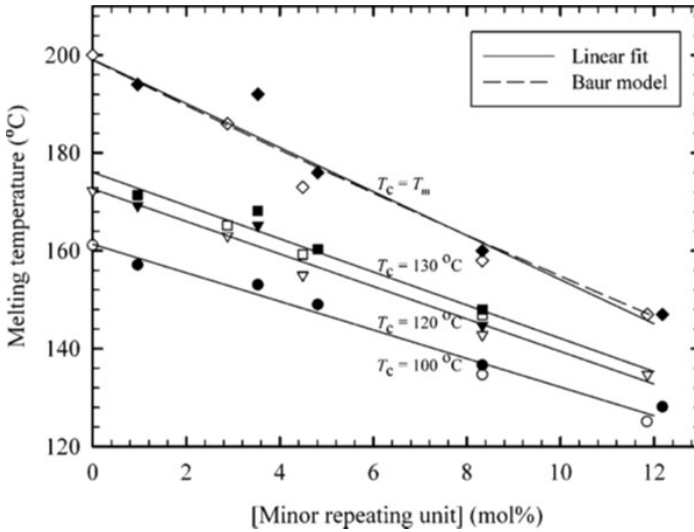


Fig. 2.9 T_m of PLA as a function of D-lactide content (minor repeating unit) for different T_c , filled symbols for PDLA and open symbols for PLLA¹, taken from [46].

Figure 2.9 allows the estimation of the equilibrium melting temperatures (T_m°). These T_m° values provide a theoretical reference for evaluating the melting temperature of a perfect and infinite crystal. In the context of Figure 2.9, T_m° is not directly measured but extrapolated using the Hoffman–Weeks method [52]. This method consists in plotting the experimentally measured T_m values as a function of T_c and extrapolating the resulting curve until it intersects the curve $T_m = T_c$. The point of intersection corresponds to the estimated T_m° and reflects the melting point of an ideal crystal formed under equilibrium conditions. For PLA, T_m° is typically estimated between 190°C and 200°C, with most values converging around 195°C for the α -form [46].

As further illustrated in Figure 2.10, the melting temperature is strongly dependent on the number-average molar mass (M_n), particularly in the low molar mass range. At low M_n , a high density of chain ends disrupts the crystalline order, resulting in reduced T_m . As M_n increases, these end-

¹Baur model will not be discussed here.

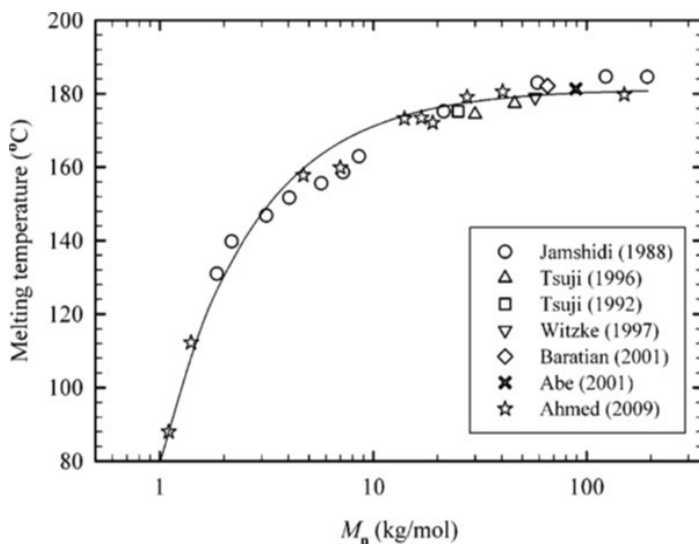


Fig. 2.10 T_m of PLA as a function of number average molar mass, taken from [46].

group effects diminish, and the melting temperature gradually approaches a plateau, reflecting the thermodynamic limit of lamellar stability.

2.5.3 Transition from disordered to ordered crystal during melt

The melting behavior of PLA is governed by complex thermal transitions that arise from a combination of solid-state reorganization [53] and melt-mediated recrystallization [54] phenomena. Both Zhang et al. and Androsch et al. demonstrated that the structural form initially adopted during crystallization significantly influences the subsequent melting pathway. At low crystallization temperatures, PLA tends to form disordered crystals (α'), which upon heating, undergo a disorder-to-order transition before melting. This transformation manifests as a small exothermic peak in DSC curves around 160°C , as represented by T_{exo} in Figure 2.11. This figure combines representative DSC heating curves of PLA crystallized at various temperatures (left), where T_{m1} corresponds to the melting of disordered α' crystals and T_{m2} to the melting of more ordered α crystals. The intermediate exothermic peak reflects the transition from α' to α . To better illustrate this

phenomenon, Figure 2.11 (right) shows the evolution of melting temperatures with the crystallization temperature, indicating the thermal conditions under which the α' to α transformation occurs. This is particularly observed below 110°C, where the exothermic peak precedes the α' -crystals melting, confirming that the α' to α transition proceeds via a solid-state mechanism under these conditions. The gradual disappearance of this peak with increasing crystallization temperature marks the evolution toward more ordered crystalline structures. Zhang et al. further confirm those results by WAXD measurements showing the structural reorganization from the metastable α' phase to the more ordered α form [53].

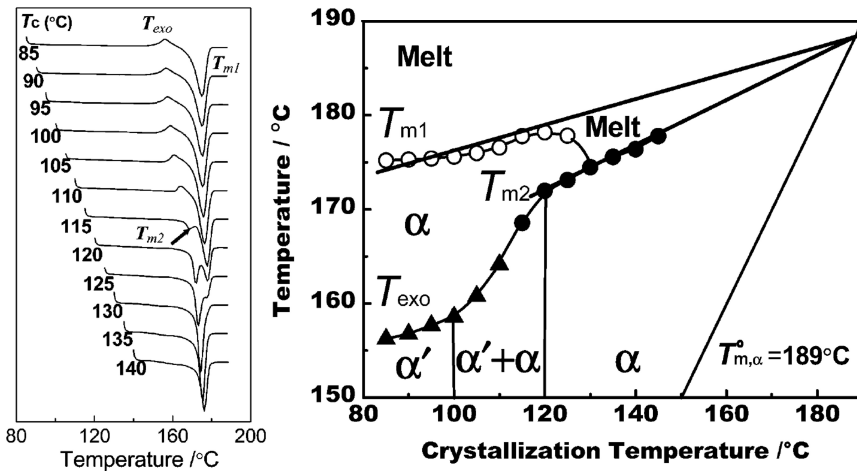


Fig. 2.11 DSC heating curve of PLA crystallized at different temperatures (Left). Characteristic temperatures (T_{m1} , T_{m2} and T_{exo}), taken from DSC heating curves, plotted versus T_c , adapted from [53].

In contrast to this solid-state mechanism, Figure 2.12 illustrates the thermal behavior of samples initially containing the α' -phase during annealing using ultra-fast heating by flash differential scanning calorimetry (fDSC). With increasing annealing time, though still within a short timescale, the melting endotherm progressively shifts and sharpens, indicating that the transformation from α' to α occurs through a melt-mediated recrystallization process. This mechanism, observed under very high heating rates, involves the partial melting of the disordered α' -crystals, followed by rapid recrystallization into more stable α -crystals. The fast thermal input prevents

solid-state rearrangement and favors a transition pathway via the molten state, driven by residual lamellar structures that act as self-nucleating sites.

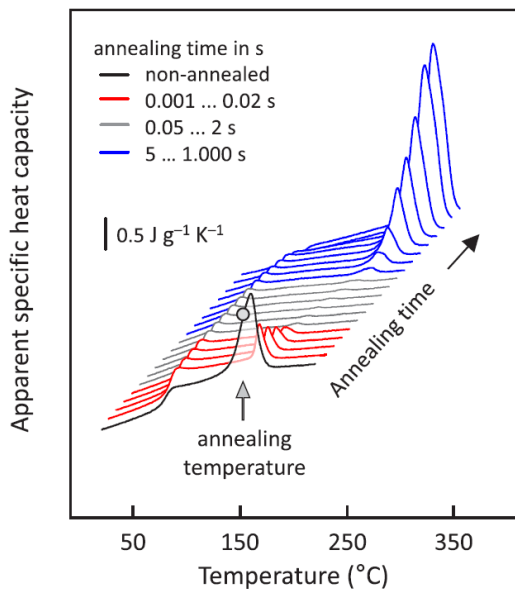


Fig. 2.12 DSC heating curves of PLA crystallized at 95°C for 400s and annealed for different periods of time at 152.5°C, taken from [54].

These findings jointly demonstrate that the α' to α transition in PLA proceeds via two kinetically distinct mechanisms depending on heating rate: a solid-state rearrangement under slow heating and a melt-mediated recrystallization under rapid heating. Both pathways represent a reorganization from a metastable disordered structure toward a more thermodynamically favorable crystalline form. Therefore, PLA melting is best described as a multi-step, condition-dependent process, governed by thermal history, crystallization conditions and chain mobility.

2.5.4 Nucleation and spherulitic growth of PLA

Experimental investigations on the isothermal crystallization of PLA have revealed the complex interplay between nucleation density and spherulitic growth rate as functions of temperature and molecular characteristics. This

section is based on a set of experimental observations compiled in the review by Saeidlou et al. [46], where the nucleation and spherulitic growth behavior of PLA was investigated using polarized optical microscopy (POM) and differential scanning calorimetry (DSC) under isothermal conditions.

2.5.4.1 Nucleation density and spherulitic morphology

The spatial distribution and density of nuclei formed during PLA crystallization depend strongly on the crystallization temperature. As shown in Figure 2.13, the nucleation density increases with decreasing T_c , due to the enhanced supercooling that facilitates the formation of new nuclei. This strong temperature dependence leads to significant variations in spherulitic morphology.

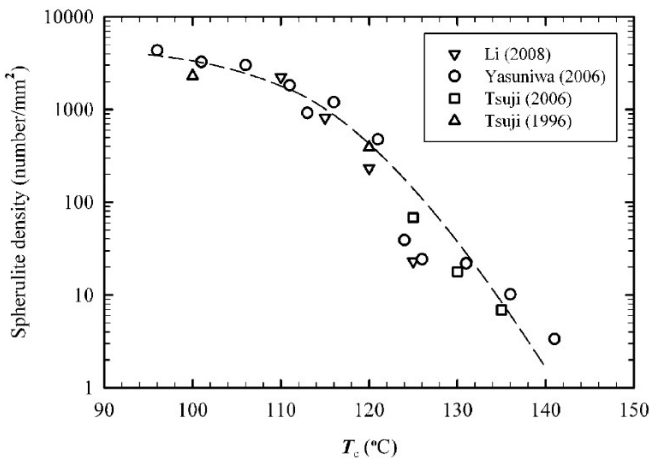


Fig. 2.13 Spherulite density of thin polymer films as a function of crystallization temperature, taken from [46].

Polarized optical microscopy provides direct insight into these morphological differences. At low crystallization temperatures, the nucleation density is high, resulting in numerous small spherulites whose radial growth is eventually constrained by impingement with neighboring structures. In contrast, at higher temperatures, the number of nucleation sites decreases significantly, yielding fewer but much larger spherulites. The final morphology is therefore governed by the balance between nucleation frequency and the available space for radial growth. These morphological differences are clearly visible in Figure 2.14, which shows POM micrographs of PLA

crystallized at different temperatures.

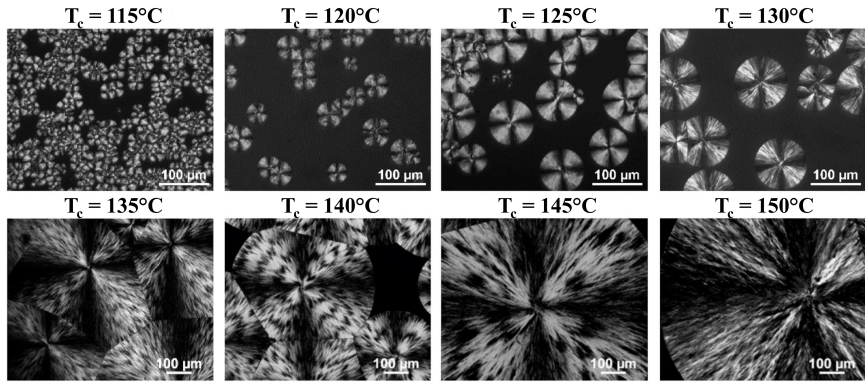


Fig. 2.14 POM images of spherulitic morphologies of PLA isothermally crystallized at different T_c , adapted from [27].

These images are adapted from the work of Safandowska and Rozanski [27], who reported that in neat PLA, spherulites appear mostly non-banded with well-defined Maltese-cross patterns. Banded morphologies were only observed within a narrow crystallization temperature window (135°C to 145°C). At lower temperatures, the high density of nuclei and rapid radial growth inhibit the regular lamellar twisting required for band formation, leading to the formation of a large number of non-banded spherulites. Conversely, at higher temperatures, although the nucleation density is extremely low, banded spherulites are no longer observed. While not explicitly discussed by the authors, this could result from the markedly slow radial growth at such high crystallization temperatures, as the thermodynamic driving force becomes too small to sustain regular lamellar twisting, in agreement with general crystallization kinetics, as explained in the previous theoretical section.

In addition to T_c , Jalali et al. [55] showed that thermal pre-treatments such as self-nucleation can also enhance nucleation site density, by leaving residual crystalline fragments that act as effective nucleating agents. Moreover, Androsch and Di Lorenzo [56] demonstrated that PLA is capable of nucleating even below its glass transition temperature, indicating that the formation of nuclei is not restricted to the rubbery state. This conclusion

was based on an indirect calorimetric approach: PLA samples were first aged isothermally at sub- T_g temperatures, then crystallized at 393K. An increase in the enthalpy of crystallization following aging was interpreted as the signature of nuclei pre-formed during the sub- T_g treatment. It is worth noting that it does not provide a direct morphological or structural characterization of the nuclei. Consequently, the interpretation relies on the assumption that changes in crystallization kinetics stem exclusively from prior nucleation events, which may overlook alternative mechanisms.

2.5.5 Growth rate and influence of temperature and molar mass

The spherulitic growth rate (G) can be experimentally determined from polarized optical microscopy by measuring the radial expansion of individual spherulites as a function of time during isothermal crystallization. This direct method allows precise quantification of crystal growth dynamics.

As discussed in the theoretical section, G shows a non-monotonic, bell-shaped dependence on crystallization temperature. This trend has been confirmed by Safandowska and Rozanski [27], who reported G_{max} of $2.50 \mu\text{m}/\text{min}$ at 125°C , illustrated in Figure 2.15.

The influence of molar mass has also been extensively studied and is highlighted in Figure 2.16. Lower molar masses consistently lead to higher spherulitic growth rates, especially in the vicinity of the temperature range where G reaches its maximum. This behavior is attributed to the enhanced chain mobility and reduced entanglement density of shorter chains, which facilitate their incorporation into the crystalline phase.

While POM offers a local and morphological view of growth kinetics, differential scanning calorimetry (DSC) provides a complementary global perspective by capturing the bulk crystallization behavior. One of the most widely used kinetic parameters obtained from isothermal DSC measurements is the half-crystallization time ($t_{1/2}$), which reflects the time required to reach 50% of the crystallization enthalpy. Although it does not directly correspond to G , $t_{1/2}$ encompasses the combined effects of nucleation and growth.

Figure 2.17 presents a compilation of $t_{1/2}$ values for neat PLA with

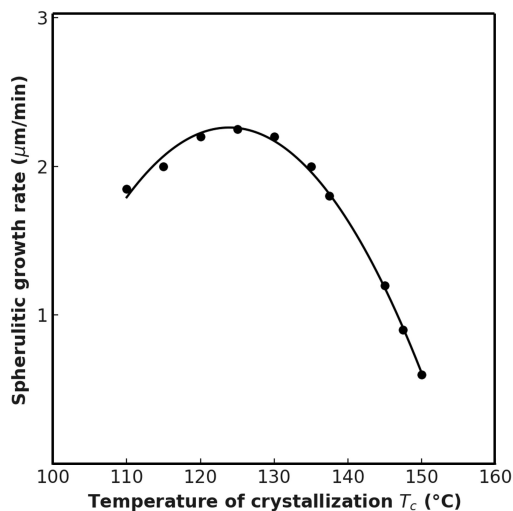


Fig. 2.15 Spherulitic growth rate of PLA depending on T_c , adapted from [27].

varying molar masses and D-lactide contents. The data show a bell-shaped dependence on temperature, with a minimum typically located around 110 $^{\circ}\text{C}$ for pure PLA, in agreement with the temperature range for maximum G values. Moreover, the half-crystallization time is systematically shorter for lower molar mass PLA, confirming the faster crystallization kinetics in these systems.

Studies by He et al. [57] and Pan et al. [58] corroborated these trends: He et al. showed that spherulitic growth is significantly enhanced in samples with reduced molar mass across a range of crystallization temperatures, while Pan et al. emphasized that this effect becomes particularly pronounced near the optimal crystallization window. Both studies confirm that lower molar mass PLA samples exhibit shorter $t_{1/2}$ values, supporting the conclusion that molar mass is a critical factor in crystallization kinetics.

Saeidlou et al. [46] summarized it by highlighting that the crystal growth rate in polymers is governed by both thermodynamic and kinetic factors. The growth rate tends to increase with decreasing molar mass due to enhanced segmental mobility, which facilitates the transport of chains toward the crystallization front. However, this growth is also limited by the temperature-dependent interplay between the thermodynamic driving

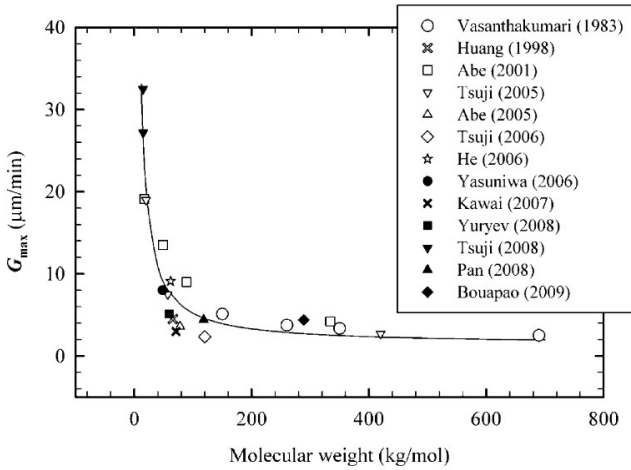


Fig. 2.16 Maximum spherulite growth rate as a function of molar mass, taken from [46].

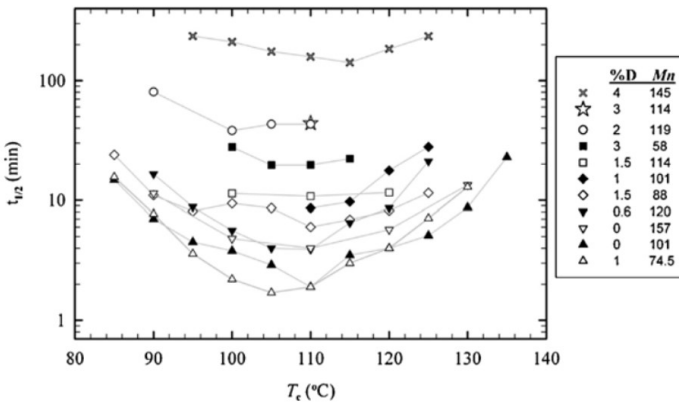


Fig. 2.17 Crystallization half-time as a function of crystallization temperature for different D-lactide content and molar masses, taken from [46].

force for crystallization and the ability of chains to diffuse: at lower temperatures, crystallization becomes more favorable, but molecular mobility decreases, restricting the arrival of chains at the growing crystal interface.

2.5.6 Mechanical properties of PLA

Regarding other biocompatible polymers, PLA is widely recognized for its high tensile strength and modulus, which are essential for applications requiring structural integrity. These mechanical properties make PLA a promising candidate for biomedical uses such as scaffolds, implants and sutures. However, PLA also suffers from significant limitations in mechanical behavior: it is inherently brittle, with poor impact resistance and low elongation at break, which restricts its ability to undergo deformation without failure [12]. These issues pose challenges in load-bearing or dynamic environments where flexibility, toughness and durability are critical. As such, enhancing the mechanical profile of PLA is required for expanding its use in biomedical applications.

From a mechanical standpoint, PLA's elastic modulus, tensile strength, and elongation at break are sensitive to both its molecular characteristics, such as molar mass or D-isomer content, and its processing history. Perego et al. [59] and Yang et al. [60] have conducted extensive studies on the influence of molar mass, thermal treatments and crosslinking on mechanical performance of PLA. Unmodified PLA, in its as-processed state, typically shows a Young's modulus between 1.7 and 3.8 GPa, a tensile strength ranging from 59 to 66 MPa, and an elongation at break below 10%. Tensile tests confirm that increasing the molar mass tends to improve the modulus and strength, while post-crystallization through annealing further enhances stiffness but reduces ductility.

Different strategies have been proposed to improve the mechanical properties of PLA. Perego et al. [59] showed that higher molar masses combined with thermal annealing can raise the crystallinity to 40–45%, resulting in greater stiffness but lowering the elongation at break. Yang et al. [60] introduced chemical crosslinking as a means to improve mechanical stability and thermal resistance. Despite a slight reduction in crystallinity, crosslinked PLA exhibited increased modulus and tensile strength, indicating that the formation of a network structure compensates for the reduction in crystalline order. A comparative summary of mechanical properties from these studies is presented in the table 2.1.

Although improving mechanical properties through molar mass increase, annealing or crosslinking leads to incremental gains, these strategies alone are insufficient to overcome the brittleness and limited impact per-

Table 2.1 Mechanical properties and crystallinity of various PLA types as reported in the literature. For the samples studied by Perego et al. (marked with an asterisk *), crystallinity values were not explicitly provided; they were estimated by normalizing the reported enthalpies of crystallization using the reference enthalpy value from Yang et al. to allow consistent comparison.

Type of PLA	M_n [g/mol]	E [GPa]	$\sigma_{\max}$ [MPa]	ε_b [%]	χ_c [%]
Neat PLA [59]	23 000	3.6	59	1.5	6*
Neat PLA [59]	67 000	3.8	59	7	2*
Neat PLA [60]	-	1.7	66	9	32
Annealed PLA [59]	20 000	4.1	47	1	48*
Annealed PLA [59]	71 000	4.2	66	4	31*
Crosslinked PLA [60]	-	1.9	75	7	24

formance of PLA. More substantial improvements typically require modification at the material composition level. Nofar et al. [61] provided a comprehensive review of PLA-based blends with other polymers, which have shown considerable improvements in elongation at break and toughness while maintaining biodegradability. These blends are particularly effective in addressing the intrinsic brittleness of neat PLA.

Similarly, Saini et al. [12] emphasized that polymer blending strategies can be tailored not only to enhance mechanical performance but also to adjust degradation profiles, which is crucial in biomedical contexts such as controlled drug delivery or tissue scaffolding. In addition to blending PLA with other polymers, they also discussed the incorporation of natural materials which offer biocompatibility and bioactivity enhancements while also modulating the mechanical response of the resulting composites.

2.5.7 PLA in biomedical applications

One of the most widely explored fields where PLA has been implemented is the fabrication of porous scaffolds for tissue engineering. These scaffolds are designed to provide temporary support for cell proliferation and extracellular matrix deposition. Thanks to its ease of processing and compatibility with melt-based manufacturing, PLA has been extensively used to produce such structures, especially via extrusion-based additive manufacturing techniques. Fused deposition modeling (FDM), in particular, has played a central role due to its capacity to generate customized scaffolds with controlled macro-architecture [9, 10]. Nevertheless, the use of unmodified PLA in these systems typically results in limited bioactivity and poor cell adhesion due to its hydrophobic surface and lack of biochemical functionality [62].

Similarly, in orthopedic applications such as biodegradable screws and fixation devices, PLA has been used for its stiffness and its resorption capacity, which eliminates the need for secondary surgical removal. However, its brittleness and low impact resistance restrict its use to applications with limited mechanical stress and long-term integrity is often compromised in hydrated environments [63]. For drug delivery systems, PLA has been employed to create biodegradable carriers, such as microparticles or implantable matrices, capable of providing sustained release of hydrophobic compounds. Yet again, its slow and acidic degradation profile, combined with limited solubility control, restricts its versatility for more advanced therapeutic applications [62].

Across these application domains, the recurring limitations of neat PLA, namely poor toughness, slow degradation, hydrophobic surface chemistry and limited functionalization capacity, underline the necessity for material improvement. In this context, two main strategies have emerged: the chemical or physicochemical modification of PLA and the development of blends and composite systems. These approaches aim to overcome the intrinsic material limitations not by changing the application but by tailoring the polymer to better fulfill structural and functional requirements.

To expand the utility of PLA in biomedical contexts, extensive efforts have been made to tailor its surface and bulk properties to meet the functional requirements of specific applications. Surface modification techniques have been widely employed to improve the biointerfacial performance of PLA, particularly in scaffold-based tissue engineering. Since native PLA

lacks cell-recognition motifs and presents a hydrophobic surface that inhibits protein adsorption and cell adhesion, treatments such as plasma activation or surface coating have been used to introduce reactive groups and increase surface wettability [9, 10]. These modifications facilitate the subsequent immobilization of bioactive molecules, thereby improving cell attachment and tissue integration.

In parallel, the incorporation of hydrophilic segments through copolymerization, particularly with poly(ethylene glycol) (PEG), has enabled the design of PLA-based materials with improved hydrophilicity and degradation kinetics [62]. Such amphiphilic copolymers are commonly used in nanoparticle drug delivery systems. In load-bearing contexts, copolymerization with more flexible or ductile polymers like polycaprolactone (PCL) has been explored to address the brittleness of PLA, yielding materials with enhanced elongation and impact resistance while maintaining resorbability [63]. These modifications are not ends in themselves, but are driven by specific functional challenges arising in biomedical use: improved cell-material interactions in scaffolds and controlled degradation in implants. As such, the chemical or physical modification of PLA serves as a material-level response to the performance limitations revealed by its clinical and experimental deployment.

In addition to chemical modifications, another widely adopted strategy to overcome the intrinsic limitations of PLA is the formulation of blends and composites. These systems combine PLA with other polymers, such as poly(ethylene glycol) (PEG), polycaprolactone (PCL), polyhydroxybutyrate (PHB), poly(butylene adipate-*co*-terephthalate) (PBAT) or natural macromolecules like chitosan, gelatin or hydroxyapatite, to create materials with enhanced toughness, improved hydrophilicity or accelerated degradation profiles [12, 64]. The resulting blends often exhibit synergistic properties that neither component possesses individually. In bone tissue engineering, for instance, the blending of PLA with bioceramics such as hydroxyapatite or tricalcium phosphate has enabled the fabrication of scaffolds with improved osteoconductivity and mechanical reinforcement [9].

In the context of drug delivery, blending with PEG or other amphiphilic polymers allows finer control over drug release kinetics. The use of PLA blends is also closely associated with additive manufacturing technologies: the ability to produce customized, hierarchical and highly porous structures via FDM or melt electrospinning has been essential in extending the material's applicability to complex therapeutic architectures [10]. In this context,

polymer blending, such as PLA/PEG or PLA/PCL, offers additional control over mechanical behavior and degradation rates, enabling the design of scaffolds tailored to specific tissue types or loading conditions. While the design and performance of PLA-based blends will be discussed in greater detail in the following section, their relevance here lies in illustrating how material combinations have become essential to compensate for the shortcomings of neat PLA in demanding biomedical environments.

3

PLA/PEG blends

As highlighted in the previous section, PLA alone, despite its biocompatibility and biodegradability, does not fully meet the requirements for many biomedical applications. Its brittleness, limited hydrophilicity and slow crystallization behavior often make it unsuitable on its own for complex scaffolding or implant applications. One of the most effective ways to overcome these limitations is to blend PLA with a second polymer, carefully selected to bring in complementary features.

3.1 PEG overview

Poly(ethylene glycol), or PEG, has emerged as a particularly promising candidate in this context. Widely used and FDA-approved, PEG combines several attributes that make it ideal for biomedical use as its hydrophilicity, high flexible structure and biocompatibility. But more importantly, it plays an active role in modifying both the structure and performance of PLA-based materials. When blended with PLA, it softens the material by increasing chain mobility, lowers the glass transition temperature and enhances flexibility [13], making the blended material easier to process. This plasticizing effect can be precisely tuned simply by adjusting the PEG content [65].

One of the key benefits of PEG lies in its molecular tunability. Its physical form can be a liquid or a soft crystalline solid and is tailored simply by selecting the appropriate molar mass [66]. Therefore, it has a T_g ranging from -98°C to -17°C and a T_m from 51°C to 68°C , while its T_c is approximately 40°C . This allows for precise control over blend properties and processing conditions.

For the fabrication of scaffolds, PEG serves more than one role. It can improve hydrophilicity, introduce porosity and make the surface more favorable to cell adhesion. While partially miscible with PLA, it can trigger phase separation during processing, leading to a two-phase morphology. If PEG is later removed, this morphology can be exploited to create controlled porosity [67]. This porosity can be tailored through simple adjustments in PEG content, offering a powerful and scalable method to create scaffolds with tunable architecture and biological functionality.

Rather than modifying PLA through complex chemistry, blending it with PEG offers a simple yet powerful way to tune mechanical performance, degradation rate and porosity, three critical parameters for designing functional biomaterials.

3.2 Phase separation in polymer blends

3.2.1 Miscibility of polymer blends

Blending polymers is far from a straightforward process. Depending on the nature of the components, some blends exhibit full miscibility due to favorable intermolecular interactions, while others undergo complete phase separation driven by the low mixing entropy and strong repulsive forces between chains. In many cases, partial miscibility results in complex phase morphologies that must be understood to control the final properties of the material.

The miscibility of two polymers depends primarily on their thermodynamic compatibility, which is often evaluated using the Flory-Huggins theory. This model describes the Gibbs free energy of mixing per unit volume as a function of the volume fractions and the degrees of polymerization

of each component, as well as an interaction parameter. In its classical form, the Flory-Huggins equation is expressed as:

$$\Delta G_{mix} = \frac{RT}{v_0} \left(\underbrace{\frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B}_{\text{entropic}} + \underbrace{\chi \phi_A \phi_B}_{\text{enthalpic}} \right) \quad (3.1)$$

where ϕ_A and ϕ_B are the volume fractions of polymers A and B, N_A and N_B are their respective degrees of polymerization, and χ is the Flory-Huggins interaction parameter. The term v_0 represents the molar volume of a reference segment, typically corresponding to the volume of a repeating unit in the polymer lattice.

This equation highlights the low entropy of mixing typically observed in polymer blends, due to the large size of the macromolecular chains, making the enthalpic contribution, governed by χ , decisive for miscibility. The parameter χ can be estimated from the solubility parameters of the two polymers using the relation [68]:

$$\chi = \frac{V_{ref}}{RT} (\delta_A - \delta_B)^2 \quad (3.2)$$

where δ_A and δ_B are the solubility parameters of each component and V_{ref} is the molar volume of a reference structural unit, usually taken as the molar volume of a monomer segment or an average repeat unit. This formulation emphasizes that miscibility is favored when the solubility parameters of the two components are close [68]. A low value of χ indicates favorable interactions and promotes miscibility, while a higher value typically leads to phase separation. Despite its simplified form, this expression provides a useful predictive framework for assessing the compatibility of polymer blends. However, it should be noted that the solubility parameter decreases slightly with increasing molar mass [69].

3.2.2 Liquid-liquid and liquid-solid phase separation

In binary polymer blends, phase separation may proceed through different mechanisms depending on the thermodynamic path and kinetic constraints. Two main types are typically distinguished: liquid-liquid (LL) separation and liquid-solid (LS) demixing. LL separation occurs entirely within the amorphous state, either through spinodal decomposition or nucleation

and growth, depending on whether the system lies within the unstable or metastable region of the phase diagram. Spinodal decomposition leads to spontaneous amplification of composition fluctuations and results in interconnected morphologies, while nucleation-based demixing gives rise to dispersed domains of the minority phase, as presented on Figure 3.1.

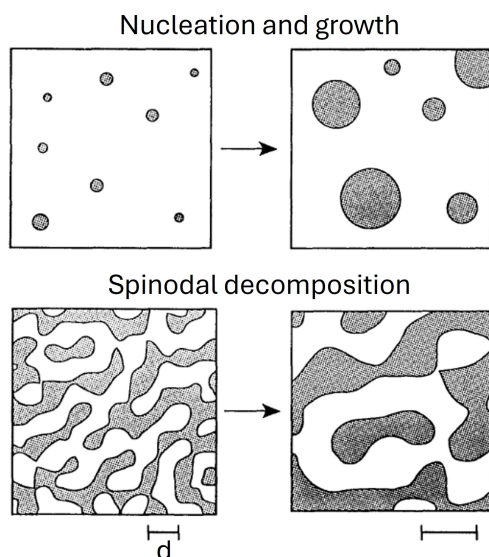


Fig. 3.1 Comparison of amorphous blend morphology between nucleation-growth and spinodal decomposition, with d an arbitrary length used as scale, adapted from [69].

Importantly, LL demixing is the regime that can be quantitatively addressed using Flory–Huggins theory. In this framework, the interaction parameter χ serves as a predictive tool to identify conditions under which homogeneous mixing becomes thermodynamically unfavorable, leading to phase separation within the amorphous phase.

LS demixing, by contrast, involves crystallization of one polymer component. As the crystalline phase forms, the remaining amorphous components, in the liquid state, are expelled generating local composition gradients and potentially triggering secondary phase separation. This mechanism is particularly significant in systems where crystallization kinetics outpace diffusion,

such that excluded species accumulate ahead of the crystallization front.

The coupling between crystallization and phase separation was described by Keith and Padden in the context of spherulitic growth [70]. According to their model, the rejection of impurities at the advancing front of a spherulite leads to an increase in local concentration of the amorphous components. When this concentration exceeds the miscibility threshold, phase separation can be induced locally, even if the global blend remains macroscopically miscible. This phenomenon, referred to as secondary phase separation, alters the morphology around growing spherulites and may significantly influence the final structure of the material.

An important insight from the Keith and Padden theory is the relationship between the interfacial thickness δ ahead of the growth front and the crystallization kinetics. Specifically, δ is governed by the ratio D/G where D is the diffusion coefficient of the amorphous component and G is the growth rate of the crystalline front. A high growth rate or a low diffusivity results in a narrow accumulation zone (δ small), where rejected chains are confined to a limited volume. This confinement can lead to sharp concentration gradients and locally elevated impurity levels, potentially exceeding the miscibility threshold and inducing localized phase separation.

However, rapid crystal growth also reduces the time available for impurity diffusion. When the excluded species, considered as impurities, are insufficiently mobile, a significant fraction may become trapped within the growing crystalline structure. These species are typically incorporated into the interlamellar amorphous regions of the crystallizing polymer, where they may remain either as isolated chains dispersed within the amorphous matrix, or as small aggregates depending on their affinity and local concentration. This partial entrapment can limit the extent of accumulation ahead of the front, thereby reducing the likelihood of localized phase separation in the surrounding melt. At the same time, the presence of such impurities within the amorphous domains can interfere with lamellar organization, influence the regularity of the crystalline texture and ultimately affect the kinetics and morphology of the crystallization process itself.

3.2.3 Typical phase diagram of polymer blends

A typical phase diagram for a binary polymer blend, such as the one shown in Figure 3.2, reveals critical information about the thermodynamic stability of the system as a function of temperature and composition. The diagram features two miscibility boundaries: the Upper Critical Solution Temperature (UCST) and the Lower Critical Solution Temperature (LCST), each forming a closed-loop envelope. These curves delimit the region within which the system exhibits phase separation. Between the UCST and LCST lies the single-phase region, where the blend remains homogeneously mixed under all conditions.

The presence of both UCST and LCST reflects a temperature-dependent inversion of the interaction parameter χ . When χ increases with increasing temperature, the blend is miscible only at low temperatures, which is characteristic of LCST-type behavior. Conversely, when χ decreases as the temperature increases, miscibility is favored only above a certain temperature, corresponding to a system exhibiting an UCST.

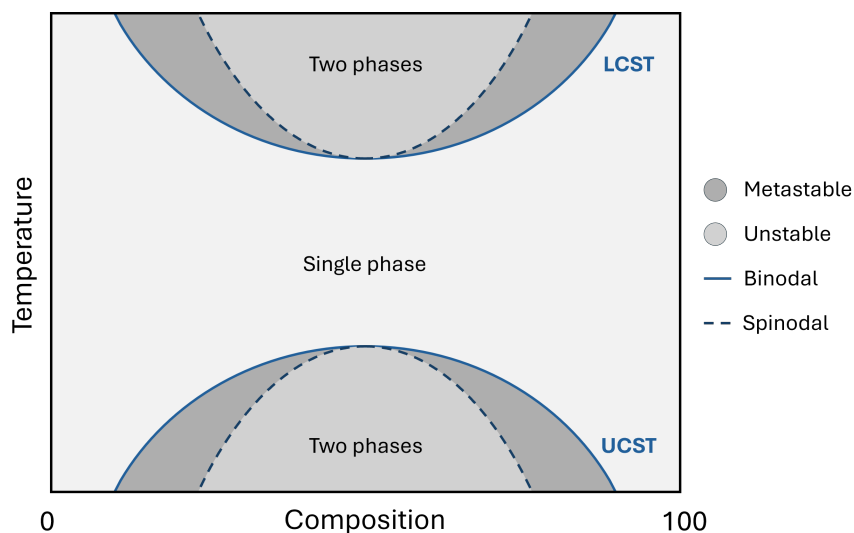


Fig. 3.2 Theoretical phase diagram for binary polymer blend, redrawn from [71].

The bimodal curves define the limits of thermodynamic miscibility and

separate the single-phase region from the two-phase region. Within the area enclosed by the bimodal, the system is in a metastable state: it can remain macroscopically homogeneous, but phase separation may still occur if a sufficiently large fluctuation or an impurity triggers nucleation. This leads to a demixing process governed by nucleation and growth.

Deeper inside the phase-separated region, the system enters the spinodal region, which is delimited by the spinodal curves. Here, the blend is intrinsically unstable: spontaneous fluctuations in local composition, at the molecular level, lead to phase separation. Those fluctuations grow continuously and gives rise to spinodal decomposition, a mechanism that typically produces interconnected-bicontinuous morphologies [71].

Beyond this thermodynamic framework, additional complexity arises in semi-crystalline systems, where crystallization introduces local concentration gradients that are not taken into account in the equilibrium diagram. As one component crystallizes, the expulsion of the non-crystallizing species can locally alter the composition of the surrounding melt, effectively shifting it into regions of the diagram associated with immiscibility. While the diagram does not explicitly represent crystallization phenomena, it remains a valuable reference for anticipating how such local variations may influence the spatial distribution of phases. In this way, the phase diagram, when interpreted with kinetic and structural considerations, can help to understand the development of the final morphology in polymer blends.

3.3 Phase separation and miscibility for PLA/PEG blends

Understanding the miscibility between PLA and PEG is essential for interpreting the spatial distribution of PEG within the PLA matrix during phase transitions, particularly crystallization. The degree of miscibility directly influences whether PEG remains dispersed in the amorphous phase, is excluded during crystallite formation or participates in phase-separated domains, thereby shaping the final morphology and functional properties of the blend.

The miscibility of PLA and PEG blends has been primarily assessed through thermal analysis techniques, with particular emphasis on the evolu-

tion of the glass transition temperature. In polymer blends, the detection of a single T_g intermediate between those of the two components is commonly interpreted as an indicator of miscibility within the amorphous phase. This behavior is often evaluated using the Fox equation [72]:

$$\frac{1}{T_{g,blend}} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (3.3)$$

where w_i and $T_{g,i}$ represent the weight fraction and glass transition temperature of component i . This equation is actually a simplified form of the more general Couchman model [73], which assumes comparable heat capacity changes and relatively close T_g values between the two components. Although theoretical predictions from this equation may diverge from experimental values, it remains a useful tool to capture compositional trends. In particular, the T_g of a blend tends to approach that of the major component and the observation of a single, composition-dependent T_g can be considered indicative of microscopic amorphous miscibility. Whereas the apparition of two distinct T_g is related to two immiscible components.

However, this approach has limitations, particularly in semi-crystalline systems where overlapping thermal events may prevent the detection of distinct transitions. It is especially the case for PLA/PEG blends where the T_m of PEG and the T_g of PLA are in the same range (around 60°C), as shown in Figure 3.3 (left). Also, the T_g may be difficult to detect because of the high crystallinity of PEG. This issue is well illustrated in the work of Younes and Cohn [74], who observed no clear single T_g in PLA/PEG blends, regardless of PEG molar mass (1500–35,000 g/mol). Instead, the melting temperature of PEG was significantly reduced, while the T_m of PLA remained largely unchanged. This asymmetry indicates that PEG is more strongly influenced by the presence of PLA than the contrary. The pronounced lowering of the PEG melting point, together with the limited effect on PLA melting behavior, indicates partial phase separation. This is especially evident in the PEG 20–30 wt% range, where a substantial increase in the PEG melting enthalpy is observed, as shown by the DSC thermograms in Figure 3.3 (right). This suggests that, beyond a certain concentration threshold, PEG is able to crystallize more extensively, likely due to the formation of PEG-rich domains within the blend. Such a morphological evolution implies microphase segregation, with discrete PEG-rich and PLA-rich regions emerging as phase separation progresses.

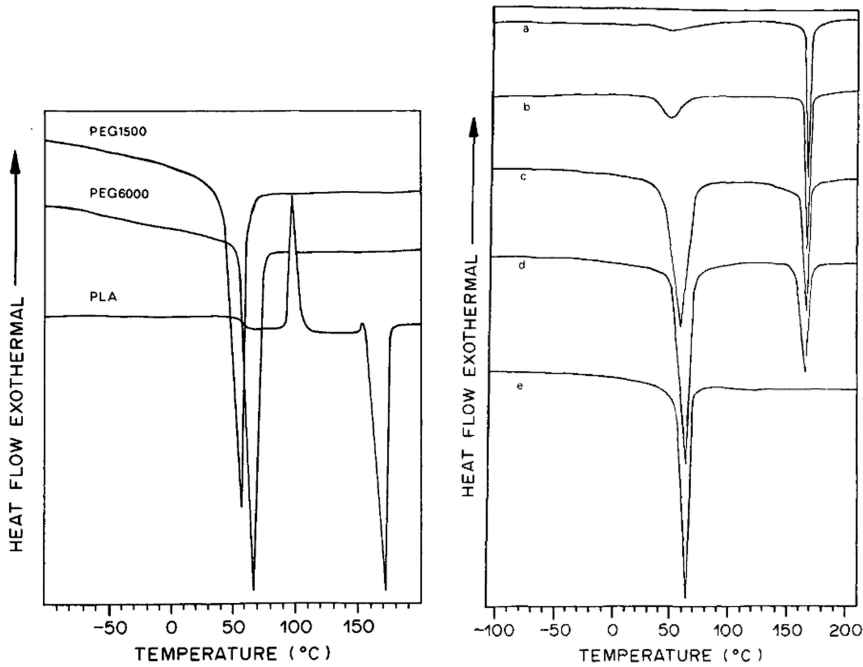


Fig. 3.3 Typical DSC curves of PLA and PEG with an overlapping of $T_{g,PLA}$ and $T_{m,PEG}$ (left panel). DSC curves of PLA/PEG blends with 10% (a), 20% (b), 30% (c), 70% (d) and 80% (e) of PEG (right panel), taken from [74].

To address such ambiguities, Nijenhuis et al. [75] employed an alternative preparation route, relying on co-precipitation of PLA and PEG from a common solvent rather than conventional solvent casting. This method promotes a better mixing prior to solidification and minimizes the risk of phase separation during slow solvent evaporation. As a result, blends containing up to 20 wt% PEG ($M_w = 800\text{--}4000$ kg/mol) exhibited a single T_g and no evidence of phase-separated domains, pointing to a higher degree of miscibility in the amorphous phase. Interestingly, despite the very high molar masses used, known to reduce miscibility [76], the blends remained homogeneous. This observation supports the idea that the partial miscibility observed in many PLA/PEG systems may not stem from an intrinsic incompatibility between the chains, but rather from the crystallization behavior of PLA, which tends to expel PEG from its growing lamellae.

A different miscibility behavior was reported by Yang et al. [77] who observed a more limited miscibility window for PLA/PEG blends prepared with PEG of lower molar mass ($M_w = 20$ kg/mol). A single, progressively depressed T_g was observed only up to 30 wt% PEG, beyond which thermal and mechanical analyses revealed clear signs of phase separation. Dynamic mechanical analysis confirmed a broadening and eventual splitting of the glass transition, consistent with the emergence of two distinct amorphous populations.

Although the exact composition threshold for phase separation may vary depending on molar mass, blend preparation, and processing conditions, numerous studies have reported the onset of immiscibility between 10 and 50 wt% PEG [65, 77, 78, 79, 80]. However, most frequently, phase separation is observed around 30 wt%, a value that appears to represent a practical upper limit for amorphous miscibility in PLA/PEG systems.

3.3.1 Influence of PEG composition on crystallization and microstructure of PLA

The crystallization behavior of PLA in the presence of PEG has been widely examined in the literature due to the numerous ways in which PEG influences both the kinetic and morphological aspects of crystallization. It modulates the crystallization of PLA through a combination of mechanisms that include changes in molecular mobility, nucleation behavior and growth dynamics [65, 77, 79, 80, 81, 82]. These effects are mediated by different parameters such as the miscibility of the components, the thermal treatment and the blend composition. Understanding the interaction of these effects is essential to understand how PLA crystallizes in the presence of PEG and how this crystallization pathway dictates the resulting microstructure, degree of crystallinity and ultimately the mechanical performance of the blend. Furthermore, identifying the precise spatial distribution of PEG within the PLA matrix is essential for predicting the porosity that can result from selective PEG extraction.

3.3.1.1 Influence of PEG on PLA crystallization kinetics

One of the most consistent observations across the literature is the plasticizing effect of PEG, which lowers the T_g of PLA and increases chain mobility. This improved segmental mobility facilitates the molecular rearrangements required for crystallization. In non-isothermal DSC experiments, when

crystallisation occurs during cooling and not during a specific isotherm, PEG-containing blends typically exhibit a lowering of the cold crystallization temperature (T_{cc}), indicating that crystallization initiates earlier during heating due to enhanced chain mobility [80]. For instance, Li et al. [80] observed that T_{cc} decreased progressively with PEG content and eventually disappeared above 10 wt%, suggesting that crystallization occurred almost entirely during the cooling stage. This behavior is closely linked to the plasticizing action of PEG, which reduces the T_g of PLA and increases chain segment mobility. Sheth et al. [79] and Wang et al. [65] reported a decrease in T_g from 57.4 °C to 42.5 °C at 10 wt% PEG ($M_w = 20\,000$ g/mol), a shift that correlates with an increase in overall crystallinity and a faster rearrangement of chains into ordered lamellae during thermal treatment.

Several studies have reported a progressive decrease in the T_m of PLA with increasing PEG content [78, 81, 75]. This reduction is typically attributed to a disturbance in the lamellar structure and a decrease in the thickness of PLA crystallites. The presence of PEG chains, mixed among the amorphous PLA chains, interferes with the regular folding and packing of PLA segments, resulting in the formation of thinner or less perfect lamellae. Nakafuku et al. [78] and Mohapatra et al. [81] observed a decrease in T_m of about 10–15 °C as PEG content increased from 0 to 30 wt%. This T_m depression is attributed to both the dilution of crystallizable PLA and to the disruption of its crystallization pathway by the flexible PEG environment. Nijenhuis et al. [75] similarly reported that the melting temperature of PLA decreased from 196 °C in the pure polymer to 190 °C at 18 wt% PEO in blends prepared by co-precipitation, supporting the idea that high molar mass PEO alters the lamellar structure of PLA crystals. As a reminder, PEO is another appellation for PEG; it is mostly used when M_w exceeds 10–20 kg/mol.

The melting temperature of PLA is also influenced by the temperature at which crystallization is carried out. According to the Gibbs–Thomson equation [83], T_m increases with lamellar thickness, which is in turn governed by T_c :

$$T_m = T_m^\circ \left(1 - \frac{2\sigma_e}{\Delta H_f \cdot \rho_c \cdot l} \right) \quad (3.4)$$

where T_m° is the equilibrium melting temperature, σ_e is the surface free energy, ΔH_f is the enthalpy of fusion, ρ_c the crystal density and l is the

lamellar thickness. At higher T_c , the critical lamellar thickness is larger, and lamellar thickening is faster, resulting in higher T_m values. Conversely, rapid crystallization at lower T_c leads to thinner lamellae and lowered melting points. Yang et al. [77], studying a 50 wt% PLA/PEG blend (PEG $M_w = 10,000$ g/mol), reported a decrease of about 5–8 °C in PLA melting temperature when the crystallization temperature was reduced from 130°C to 100°C, consistent with the formation of less stable crystalline structures under fast growth conditions.

Overall, PEG promotes faster crystallization of PLA under isothermal and non-isothermal conditions, especially at intermediate concentrations (10–30 wt%), where it acts as a true plasticizer without inducing significant phase separation.

The influence of PEG on PLA crystallization becomes particularly clear under isothermal conditions, where the kinetics can be precisely quantified. The spherulitic growth rate (G) of PLA increases with the addition of PEG, up to 50 wt% PEG in blends [77]. This acceleration of radial growth suggests that PEG facilitates chain mobility at the crystallization front. At the same time, the nucleation density tends to decrease, leading to fewer but larger spherulites. This behavior indicates that PEG promotes lamellar propagation while possibly interfering with nucleation, either by dilution of potential nucleation sites or by modifying the interfacial energy required for nucleation.

This effect is also reflected in the evolution of the half-time of crystallization ($t_{1/2}$), commonly used to quantify the global crystallization rate under isothermal conditions, including nucleation density and growth rate. A sharp decrease in $t_{1/2}$ was reported by Mohapatra et al. in PLA/PEG blends with up to 20 wt% PEG ($M_w = 6000$ g/mol)[81], confirming an acceleration of the overall crystallization rate. Similar results were obtained in blends containing 1–5 wt% PEG of higher molar mass ($M_w = 100\,000$ g/mol), where $t_{1/2}$ decreased progressively with PEG addition [84]. In both cases, the reduction in $t_{1/2}$ is attributed to the plasticizing effect of PEG, which lowers the energy barrier for chain rearrangement and enhances diffusion toward the crystalline front.

At higher PEG contents, however, the accelerating effect on crystallization becomes less pronounced and eventually reaches a plateau. While PEG

continues to influence the mobility of PLA chains, its ability to enhance crystallization diminishes due to the onset of phase separation. Beyond a certain concentration, typically above 20–30 wt%, the blend begins to exhibit dual-phase behavior, where part of the PEG remains miscible with PLA, while the rest forms a separate phase. In this regime, crystallization of PEG itself becomes detectable, and the morphology becomes increasingly heterogeneous [65, 85]. The continuity of the amorphous PLA matrix is disrupted and the presence of interfacial boundaries limits cooperative chain rearrangement, leading to a reduction in the effectiveness of PEG as a crystallization promoter.

The ability of PEG to influence the crystallization behavior of PLA depends strongly on its molar mass. Li et al. [80] showed that PEGs of intermediate molar mass (6,000–10,000 g/mol) most effectively enhanced PLA crystallization by balancing increased chain mobility with good miscibility. In contrast, very low molar masses mainly acted as plasticizers without strongly promoting crystallization, while higher molar masses (20,000 g/mol) favored phase separation and reduced the efficiency of crystallization enhancement. This trend was also observed by Nakafuku et al. [76] who indicated that high molar mass PEOs (20,000–200,000 g/mol) induced a stronger lowering of the melting temperature of PLA and disrupted lamellar organization. These results suggest that the molar mass of PEG can be used as a lever both to promote PLA crystallization and to induce phase separation.

3.3.1.2 Effects of PEG on PLA morphology and crystalline structure

The addition of PEG to PLA not only modifies the crystallization kinetics but also alters the final morphology of spherulites, notably promoting the formation of banded spherulitic structures. Observations using polarized optical microscopy (POM) have consistently shown that increasing PEG content leads to the development of larger spherulites exhibiting concentric banded patterns [76, 78, 79]. Sheth et al. [79] reported that the banded morphology became prominent at intermediate PEG contents (30–50 wt%). Those banded spherulites are shown on Figure 3.4 (a) for blends made of 50 wt% PEG. To further investigate the origin of these bands, they conducted a thermal treatment at 80°C, a temperature above the melting point of PEG but below that of PLA. After this selective melting step, the banded pattern persisted, as shown in Figure 3.4 (b), indicating that the ring structures are not directly associated with PEG crystallization but are inherent to the organization of the PLA lamellae, possibly stabilized or induced by the

presence of PEG.

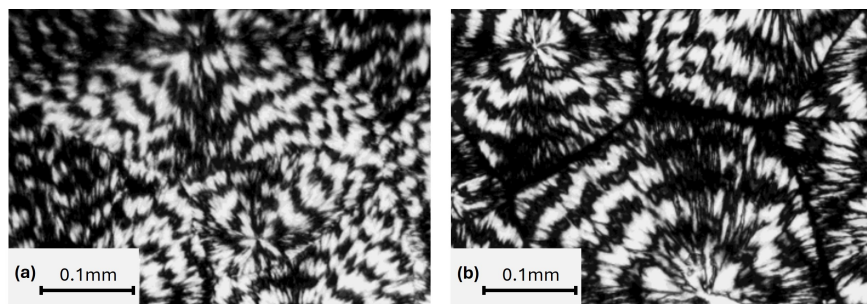


Fig. 3.4 Comparison of PLA/PEG blends with 50 wt% PEG crystallized at 130°C before (a) and after (b) reheating at 80°C, adapted from [79].

The degree of crystallinity (X_c) of PLA generally increases with PEG content up to about 20–30 wt%, reflecting the enhanced segmental mobility and facilitated lamellar thickening provided by the plasticizing effect of PEG. As PEG concentration continues to rise beyond this range, the growth of X_c tends to plateau or slightly decrease [65, 81]. This behavior results from two simultaneous effects: the dilution of crystallizable PLA segments and the onset of phase separation, which interrupts the continuity of the amorphous phase and locally impedes crystal propagation.

In parallel to the changes in crystallinity, PEG also influences the crystalline form adopted by PLA. WAXS analyses have shown that the addition of PEG favors the transition from the metastable α' -form, typically associated with rapid crystallization and lower perfection, toward the more thermodynamically stable α -form [80, 85]. This structural transition is evidenced by the narrowing of the melting endotherm observed by DSC and by the sharpening of diffraction peaks in WAXS, both indicative of improved crystalline perfection at optimal PEG contents.

3.3.2 Interactions between PLA and PEG during crystallization

Although PEG and PLA exhibit distinct crystallization behaviors, with no evidence of co-crystallization, their crystalline development remains spatially coupled. WAXS analyses have consistently confirmed that PLA and PEG form separate crystalline domains, with no new diffraction peaks

indicative of co-ordered structures [65, 85]. However, even in the absence of direct structural integration, the presence of one phase can influence the crystallization pathway of the other.

A clear illustration of such spatial interaction is provided by the work of Banpean and Sakurai [86], who showed that in blends containing 50 wt% PEG, PEG crystallization occurs preferentially within the amorphous interlamellar regions of preformed PLA spherulites. This confinement leads to a reduction in the melting temperature of PEG crystals and to the formation of thinner lamellae. Their observations suggest that the preexisting lamellar network of PLA restricts the available space for PEG crystallization, thereby steering its nucleation and growth within a confined environment, even though no molecular co-crystallization occurs between the two polymers.

In addition to these spatial effects, the chemical nature of the PEG chains also impacts PLA crystallization. Lai et al. [82] demonstrated that PEG end-groups modulate crystallization kinetics: hydroxyl-terminated PEG (PEG(2-OH)) enhances PLA crystallization more effectively than methyl-terminated PEG (PEG(2-CH₃)). The authors attributed this improvement to hydrogen bonding interactions between PEG and PLA chains, which supposedly enhance miscibility and chain mobility, facilitating lamellar organization during crystallization. However, partial attack of the ester groups of PLA by hydroxyl end groups of PEG should also have been considered, which was unfortunately not done.

3.3.3 Influence of formulation and processing conditions

The miscibility and crystallization behavior of PLA/PEG blends are primarily governed by the characteristics of the PEG component and the blend composition. Low PEG molar masses are more effective at plasticizing PLA and maintaining miscibility at moderate contents, while higher molar masses promote phase separation even at relatively low concentrations [79, 80, 84, 85]. A PEG content between 10 and 30 wt% is generally reported to enhance PLA crystallization, while higher PEG concentrations promote phase-separated morphologies and independent PEG crystallization, leading to different microstructural developments.

Thermal history, especially the cooling rate after processing, further modulates the crystallization pathway. Rapid cooling favors the formation of the α' -form of PLA and can inhibit PEG crystallization by trapping it in an

amorphous state. In contrast, slower cooling facilitates lamellar thickening, promotes higher crystallinity of PLA, and allows confined crystallization of PEG within the spherulitic structure of PLA [86].

Finally, the method of preparation can also influence phase distribution and crystallization kinetics. Co-precipitation methods, as shown by Nijenhuis et al. [75], promote better initial miscibility than traditional solvent casting or melt blending, and rapid solvent removal techniques can help to kinetically stabilize homogeneous structures [87]. However, these preparation techniques, while useful for studying the intrinsic properties of the blends under idealized conditions, may be difficult to implement in practical applications.

3.4 Mechanical properties of PLA/PEG blends

In PLA/PEG blends, the mechanical behavior arises from a complex interplay between crystallization, phase separation and molecular mobility. In most studies, the addition of PEG leads to a reduction in the elastic modulus (E) and the maximum tensile strength ($\sigma_{\max}$), while significantly enhancing the elongation at break (ϵ_b) [13, 65, 68, 80, 81, 85, 88, 89]. These trends are illustrated in Figure 3.5, where a clear decrease in tensile strength at yield (a) and in Young's modulus (b left) can be observed, together with an increase in elongation at break (b right). This behavior is commonly attributed to the plasticizing action of PEG, which softens the matrix and facilitates deformation under stress.

Despite these general trends, considerable variations in mechanical properties are observed between different studies and compositions. In particular, at high PEG contents, mechanical responses become less predictable and sometimes show totally different behavior. These discrepancies are often associated with microscopic phase separations that occur within the blends [65, 85]. When PEG domains grow beyond a critical size or lose compatibility with the surrounding PLA phase, local discontinuities and weak interfacial regions are formed. Such structural heterogeneities can act as stress concentrators, promoting premature failure and creating significant variability in tensile properties even for blends with similar compositions. This behavior is clearly reflected in the data summarized in Table 3.1, where,

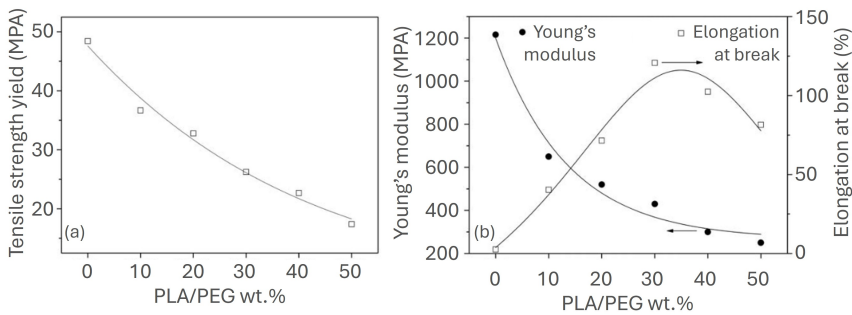


Fig. 3.5 Composition dependence of tensile strength at yield (a) and Young modulus and elongation at break (b) of PLA/PEG blends, adapted from [65].

for instance, at 20 wt% PEG, the elastic modulus ranges from 0.4 GPa to 1.3 GPa depending on the molar mass and phase distribution. Similarly, the elongation at break at 30 wt% varies widely, from less than 20% to over 400%, illustrating how microstructural inhomogeneities can dramatically affect mechanical outcomes.

The extent of phase separation, the degree of crystallinity, and the distribution of amorphous and crystalline domains are all critical factors that determine whether PEG addition results in a net improvement in toughness or a degradation of mechanical cohesion. As shown by Mohapatra et al. [81], moderate PEG additions in well-mixed systems can dramatically improve ductility without severely compromising strength, whereas at higher PEG contents or when phase separation becomes dominant, mechanical performance tends to decline. These observations underline the importance of controlling not only the blend formulation but also the processing conditions to limit phase heterogeneity and ensure suitable mechanical behavior.

3.5 PLA/PEG blends in biomedical applications

Among biodegradable polymer systems investigated for biomedical applications, blends of PLA/PEG have attracted considerable interest due to

Table 3.1 Mechanical properties of PLA/PEG blends as a function of PEG content and molar mass. Values marked with an asterisk (*) were not explicitly reported in the cited study but were estimated from the graphical data.

PEG Content [wt%]	M_w PEG [g/mol]	E [GPa]	$\sigma_{\max}$ [MPa]	ϵ_b [%]	Reference
0%	10,000	3.1	54.7	3.0	[85]
0%	6,000	3.6	38.2	2.9	[81]
0%	2,000	1.2	48.4	2.6	[65]
10%	10,000	2.7	44.4	2.8	[85]
10%	6,000	1.8	34.3	38.3	[81]
10%	2,000	0.65*	36.7	40.2*	[65]
20%	10,000	1.3	22.0	33.2	[85]
20%	6,000	0.4	23.2	330.1	[81]
20%	2,000	0.5*	32.8	71.4*	[65]
30%	10,000	0.8	11.7	17.9	[85]
30%	6,000	0.063	17.4	412.9	[81]
30%	2,000	0.4*	26.3	120.6*	[65]
40%	10,000	1.5	15.5	1.9	[85]
40%	2,000	0.3*	22.7	102.2*	[65]
50%	2,000	0.25*	17.4	81.0*	[65]

their capacity to combine structural functionality with tunable degradation and surface properties. These materials have been explored in diverse contexts such as tissue engineering [12, 13, 90], drug delivery [62], antibacterial coatings [91], injectable systems [92], and bioresorbable implants [63]. The interest in PLA/PEG combinations stems from their complementary characteristics : PLA provides structural integrity and mechanical strength, while PEG contributes hydrophilicity, flexibility, and modulation of degradation behavior.

Tissue engineering has been one of the most extensively explored domains for PLA/PEG blends. The primary challenge in scaffold design lies in developing materials that mimic the native extracellular matrix (ECM) in both architecture and function, while supporting cell adhesion, proliferation and differentiation. PLA, by itself, offers good biocompatibility and mechanical rigidity but suffers from high hydrophobicity and slow degra-

dation. PEG compensates for these limitations by enhancing water uptake, accelerating hydrolysis and improving the scaffold's cytocompatibility.

In their work, Serra et al. [13] investigated the use of PLA/PEG blends in the fabrication of three-dimensional scaffolds for tissue engineering using a low-temperature 3D printing approach, consisting in pneumatic extrusion. By incorporating PEG (400 g/mol) at 5, 10, and 20% wt into PLA matrices, they demonstrated that PEG plays multiple roles: it lowers the melt viscosity, enabling smoother and more precise extrusion during printing, it increases the surface hydrophilicity, facilitating cell attachment and it accelerates scaffold degradation by promoting water diffusion.

Salehi et al. [90] expanded on this strategy by focusing on the osteogenic potential of PLA/PEG scaffolds produced via fused deposition modeling (FDM). Their study evaluated the effect of PEG content (0–20% wt, $M_w = 6000$ g/mol) on scaffold morphology, degradation, mechanical performance and *in vitro* cell behavior. They observed that increasing PEG content led to a marked decrease in water contact angle, indicating enhanced surface hydrophilicity, and significantly accelerated scaffold degradation. In terms of biological response, higher PEG levels promoted cell adhesion and proliferation, as well as an enhanced osteogenic differentiation. Although compressive strength and elastic modulus declined with increasing PEG, particularly beyond 10 wt%, the mechanical integrity remained within acceptable ranges for bone tissue applications. Their results reinforce the notion that PEG not only functions as a plasticizer and degradation modulator but also enhances biological performance in a dose-dependent manner.

Beyond direct scaffold fabrication through extrusion, PLA/PEG blends have also been extensively employed as matrix systems in porosity-inducing techniques such as supercritical CO₂ foaming, solvent casting and particulate leaching. As reviewed by Saini et al. [12], these approaches have proven particularly effective for generating interconnected porous architectures suitable for nutrient diffusion and cell migration. PEG plays a central role in these processes by acting not only as a plasticizer, facilitating thermal processability, but also as a porogen. For example, Selvam et al. [93] demonstrated the formation of microporous PLA/PEG membranes via solvent casting and salt leaching, resulting in porous structures that supported the growth of lacrimal acinar cells. The combined effects of PEG content, molar mass and processing technique were shown to significantly influence both the structural features of the scaffold and its degradation profile.

While tissue engineering represents a primary focus, PLA/PEG blends have found utility in several other biomedical applications.

Tyler et al. [62] highlighted in their review the potential of PEG-modified PLA systems for use in controlled drug release and diagnostic applications. They noted that the inclusion of PEG can enhance the stability of the carrier in biological fluids and extend its circulation time in the body, which may contribute to a more favorable distribution profile.

Electrospun fibers based on PLA/PEG blends have also been explored for antibacterial purposes, with PEG playing a dual role in modulating mechanical flexibility and controlling the release of bioactive compounds. Such systems, as reported by Toncheva et al. [91], demonstrated favorable properties for short-term surface protection, including enhanced flexibility and rapid initial release, making them suitable for use in medical coatings or temporary barrier layers.

Microcarrier systems for cell culture and delivery also benefit from PLA/PEG blends. Kuterbekov et al. [5] developed spherulitic porous microcarriers via melt-mixing and crystallization, followed by PEG extraction. These structures supported cell adhesion, proliferation and osteogenic differentiation, making them suitable for cell culture and expansion.

In summary, PLA/PEG blends offer a synergistic integration of rigidity and flexibility, making them particularly suitable for a broad range of biomedical applications. Their capacity to integrate tunable mechanical properties, controllable degradation rates and porosity has made them particularly relevant for the design of scaffolds, drug delivery systems and biointerfaces. Beyond their intrinsic compatibility with diverse processing techniques, these systems stand out for their ability to accommodate a wide range of therapeutic needs. While various strategies have already demonstrated the potential of PLA and PEG in the fabrication of porous systems—particularly for scaffold applications, these approaches often rely on simple porosity. Yet, considering the structural and functional complexity of native biological tissues, there is a growing need to develop methods capable of generating more sophisticated, hierarchical porous architectures within these materials.

4

Controlled hierarchical porosity in 3D-printed objects

In tissue engineering, scaffold architecture must be tailored to support both biological activity and mechanical stability. Among the design parameters, porosity directly impacts cell colonization and tissue regeneration by governing the transport of nutrients, oxygen and signaling molecules, as well as the removal of metabolic waste [94]. This spatial organization defines the microenvironment encountered by cells and, in turn, influences their viability, proliferation and differentiation.

Pores within scaffolds can be broadly categorized based on their size relative to the cell. Large pores ($> 50 \mu\text{m}$), with diameters significantly exceeding that of mammalian cells, facilitate cell infiltration and vascularization, allowing for deep tissue ingrowth. In particular, pores larger than $300 \mu\text{m}$ are generally considered optimal for bone regeneration due to their ability to support neovascularization within the scaffold [95]. Pores of comparable size to the cells ($< 50 \mu\text{m}$) mainly influence adhesion and orientation at the surface or within the superficial layers of the scaffold. In contrast, small pores ($10 \text{ nm} - 1 \mu\text{m}$), substantially smaller than a cell, are perceived as surface topography rather than accessible spaces. However, these subcellular-scale features modulate protein adsorption and the initial

cell–material interactions.

Beyond pore size, the interconnectivity of the porous network is a key determinant of scaffold performance. Highly interconnected pores enable efficient nutrient diffusion and waste removal across the entire scaffold volume, which is essential to maintain cellular viability in large three-dimensional constructs. Moreover, interconnectivity ensures uniform cell distribution and facilitates the formation of a continuous extracellular matrix, ultimately promoting functional tissue regeneration. Accessible pore volume, defined as the fraction of total porosity that is reachable from the scaffold's outer surface, serves as a metric for quantifying pore connectivity and is strongly associated with the scaffold's overall efficacy.

Various fabrication strategies have been developed to introduce and control porosity in synthetic scaffolds, offering different levels of precision over architectural parameters such as pore size, spatial distribution and interconnectivity. The selected processing approach has a direct impact on the resulting scaffold morphology and, consequently, on its ability to support cellular activity and tissue formation. This underscores the importance of aligning fabrication techniques with the biological and mechanical requirements of the intended application [94].

4.1 Classic approaches to create micro-porosity

To translate architectural requirements into functional scaffolds, several well-established fabrication methods have been developed to generate microporous structures adapted to tissue engineering. These approaches rely on distinct physical or chemical principles to induce void formation within polymer matrices, resulting in porous networks that can be tailored to support the different applications needs.

4.1.1 Solvent casting and particulate leaching

Solvent casting combined with particulate leaching involves preparing a homogeneous mixture of a polymer solution and solid porogenic particles, typically water-soluble salts or sugars. The mixture is poured into a mold, and as the solvent evaporates, a solid polymer matrix forms around the dispersed particles. The structure is then immersed in water to dissolve

and remove the porogen, leaving behind a porous scaffold. The size and distribution of the pores are determined primarily by the characteristics and packing of the porogenic phase [96]. While the technique is valued for its simplicity and low cost, it often produces irregular pore shapes and limited interconnectivity. Residual solvents may remain if the drying process is not properly controlled, potentially compromising the material's safety and suitability for biomedical applications.

4.1.2 Thermally induced phase separation

Thermally induced phase separation (TIPS) is a widely employed method for fabricating microporous scaffolds by inducing the controlled demixing of an initially homogeneous system through a reduction in temperature. In its conventional form, the process consists of dissolving a polymer in a solvent with a low melting point, then cooling the solution to promote phase separation into polymer-rich and polymer-poor regions. Subsequent solvent removal, typically by sublimation, yields a porous solid whose internal architecture reflects the morphology of the separated phases [96]. Depending on the system's thermodynamic path, phase separation may proceed via nucleation and growth or spinodal decomposition, each leading to distinct pore structures. As shown by Nam and Park, [97], the quenching temperature plays a critical role in controlling the extent of domain coarsening and thus provides a means to tune both pore size and interconnectivity.

In addition to polymer-solvent systems, TIPS can also be applied to blends of two initially miscible polymers. In such systems, phase separation is not initiated by thermodynamic incompatibility but rather through the crystallization of one component during cooling. The emergence of crystalline domains induces demixing of the components, effectively resulting in a solid-liquid phase separation. As crystallization proceeds, distinct domains are formed, one rich in the crystallizable polymer and the other enriched in the second component. Upon selective extraction of the sacrificial polymer, a porous structure is obtained [8].

Thanks to its adaptability, TIPS offers precise control over scaffold microstructure by adjusting parameters such as polymer concentration, solvent composition, cooling rate and polymer crystallinity. Nevertheless, the method is best suited for generating small-scale porosity.

4.1.3 Gas foaming

Gas foaming uses a physical blowing agent, typically carbon dioxide, introduced into a polymer matrix under high pressure. Upon rapid depressurization, the dissolved gas nucleates and expands into bubbles, forming a porous structure within the solidified polymer. This solvent-free method is attractive from a biocompatibility standpoint, as it avoids the use of potentially toxic organic solvents. However, the technique tends to produce closed-cell architectures with limited pore interconnectivity, which can restrict cell migration and fluid transport. To overcome this, it is often combined with porogen leaching to introduce open channels within the structure [96].

4.1.4 Electrospinning

Electrospinning is a technique that produces nonwoven fibrous mats by applying a high-voltage electric field to a polymer solution or melt. As the charged jet is ejected and stretched, the solvent evaporates, and ultrafine fibers are deposited onto a collector, forming a porous mesh. The resulting scaffolds have a high surface-to-volume ratio and fiber diameters in the micro- to nanometer range, closely resembling the architecture of native extracellular matrix. While electrospinning offers excellent control over fiber morphology and scaffold thickness, it often relies on volatile organic solvents that must be carefully removed to ensure biocompatibility [96].

4.1.5 Freeze-drying

Freeze-drying is based on freezing a polymer solution followed by solvent removal through sublimation under vacuum. The formation of pores results from the ice crystals that act as a temporary porogen during the freezing step. Upon sublimation, these voids remain within the polymer matrix, forming a porous, sponge-like structure. The pore morphology is highly dependent on factors such as freezing rate, solvent properties and polymer concentration. Although this method avoids thermal degradation and enables the formation of interconnected networks, the resulting pores are typically small, irregular and difficult to control with precision [96].

4.1.6 Comparison of conventional microporosity fabrication techniques

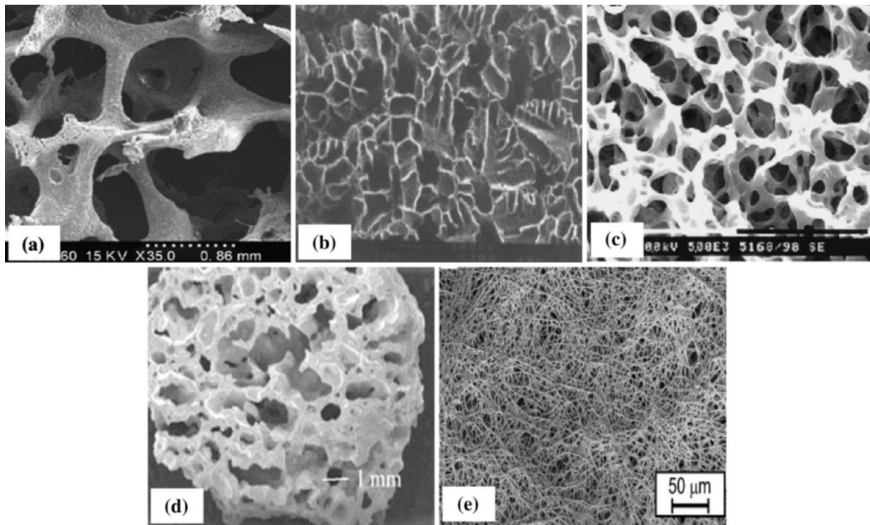


Fig. 4.1 Typical pore morphologies of porous scaffolds made by various techniques: (a) solvent casting/particulate leaching, (b) freeze-drying; (c) TIPS, (d) gas foaming and (e) electrospinning, adapted from [96].

The morphology of porous scaffolds varies significantly depending on the fabrication technique employed. As illustrated in Figure 4.1, each method yields a characteristic pore architecture that influences the biological performance and mechanical stability of the scaffold. Solvent casting combined with particulate leaching 4.1(a) typically results in an open-pore structure with relatively uniform but irregularly distributed pores. Freeze-drying 4.1(b) generates a sponge-like morphology composed of small, rounded and interconnected pores. TIPS 4.1(c) produces a network with continuous pores, whose connectivity and shape are governed by the kinetics and thermodynamics of demixing. Gas foaming 4.1(d) generally leads to large, closed and poorly interconnected pores. Electrospun scaffolds 4.1(e), in contrast, exhibit fibrous, mesh-like architectures with high surface area and nano- to microscale porosity, mimicking the extracellular matrix (ECM). Each of these morphologies presents distinct advantages and constraints in terms of nutrient diffusion, mechanical integrity and suitability for different tissue types.

Despite the diversity of approaches available, conventional techniques

Table 4.1 Main advantages and limitations of conventional microporosity fabrication methods, adapted from [96].

Technique	Advantages	Limitations
Solvent casting / particulate leaching	Simple and low-cost; tunable pore size and porosity via porogen control	Possible solvent or porogen residues; irregular and isotropic structures; poor mechanical strength
Thermally Induced Phase Separation (TIPS)	Tunable microstructure via thermodynamic and kinetic parameters; adaptable to different polymer systems	Generally limited to small pores; time-consuming and potentially partial solvent removal;
Gas foaming	Solvent-free; mild processing conditions; applicable to various polymers	Often produces closed, poorly interconnected pores; structural fragility
Electrospinning	High surface area; ECM-like fibrous architecture; adjustable fiber morphology	Thin constructs; solvent residues; not load-bearing
Freeze-drying	Formation of interconnected porous networks without high temperature; suitable for heat-sensitive materials	Small, irregular pores; difficult control over morphology; low mechanical stability

for generating microporous scaffolds share several inherent limitations, particularly when the objective is to produce complex, multiscale or patient-specific structures. In most cases, porosity is introduced during material formation, through solvent evaporation, sublimation, gas expansion or porogen dissolution, which restricts precise control over the geometry and distribution of the pores. As a result, the final architecture is often irregular and isotropic, with limited reproducibility. These methods also tend to favor the formation of small to intermediate pores, typically insufficient to support effective vascularization or deep cell infiltration in load-bearing or large-volume tissues. Moreover, because porosity is generated during material processing, shaping the scaffold into complex three-dimensional geometries is difficult. The most resulting forms are limited to simple cylinders, slabs or sponges. A comparative summary of these fabrication methods, along with their respective advantages and limitations, is presented in Table 4.1.

Achieving hierarchical porosity, defined by the coexistence of interconnected pores of different sizes and functions, remains a significant challenge when relying on a single fabrication technique. To address the limitations associated with individual methods, certain processes have been combined; for instance, gas foaming with particulate leaching [67, 97] or thermally induced phase separation (TIPS) with porogen-based approaches [8]. Such combinations not only help overcome specific constraints but also enable the generation of hierarchical porosity. Nonetheless, even these hybrid strategies show limited capability in producing scaffolds with both large interconnected pores and complex geometries, particularly when considering patient-specific architectures.

4.2 Creation of macroporosity by additive manufacturing

Additive manufacturing (AM), commonly referred to as 3D printing, has transformed the field of scaffold fabrication by enabling the production of complex, customizable geometries with high spatial precision. Unlike traditional methods that often impose limitations in shape control and pore design, AM allows for the construction of reproducible architectures with well-defined macroporous networks. Its layer-by-layer approach, based on digital models, further enables the integration of intricate internal features tailored to specific biomedical requirements.

4.2.1 Stereolithography (SLA)

Among the various additive manufacturing technologies, stereolithography (SLA) is one of the most precise methods for producing complex three-dimensional structures. As illustrated in Figure 4.2, this technique relies on the selective photopolymerization of a liquid photosensitive resin. A focused ultraviolet (UV) or visible-light laser scans the surface of the resin according to a predefined digital pattern, curing it locally to form a solid layer. After each layer is completed, the build platform is lowered to allow a new layer of resin to flow over the surface, and the process repeats until the full object is formed.

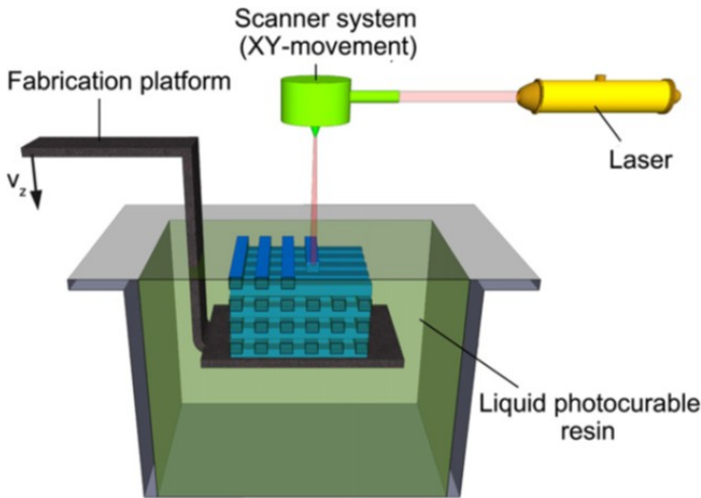


Fig. 4.2 Schematic of the SLA process, in which a focused laser selectively cures a liquid photosensitive resin to form solid layers, adapted from [98].

This layer-by-layer process allows for exceptionally high printing resolution, down to $1.2\ \mu\text{m}$ in optimized systems, making SLA particularly well-suited for fabricating scaffolds with fine structural details [96]. The method offers excellent surface finish and enables the generation of intricate, interconnected architectures with precise control over spatial geometry and pore orientation [36]. However, its application in tissue engineering remains limited by the nature of the materials involved. Most commercial resins are based on acrylate or epoxy chemistries that can release cytotoxic

by-products, necessitating extensive post-processing or the use of specially formulated biocompatible photopolymers [96]. In addition, SLA is generally restricted to photopolymerizable liquids, narrowing the range of usable biomaterials.

4.2.2 Selective laser sintering (SLS)

Selective Laser Sintering (SLS) is a powder-based additive manufacturing technique that enables the fabrication of complex porous structures without the need for support materials. As shown schematically in Figure 4.3, the process involves the deposition of a thin layer of polymer powder onto a build platform, which is then selectively fused by a high-energy laser, which traces the shape of each layer based on the digital model. After each layer is sintered, the platform lowers, a new powder layer is spread and the cycle repeats until the entire object is formed.

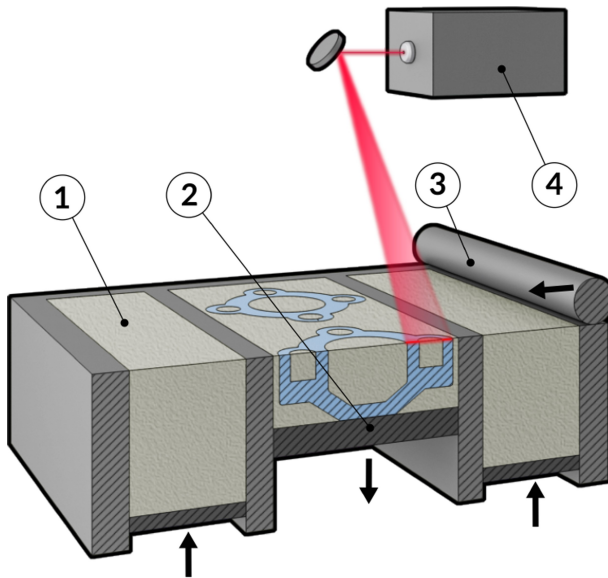


Fig. 4.3 Schematic of the SLS process where the polymer powder (1) is delivered to the build platform (2) by a roller (3), then selectively melted by a laser (4) to form the object layer-by-layer, taken from [99].

This method is compatible with a variety of thermoplastic polymers,

including biocompatible materials and allows the creation of scaffolds with well-defined macroporosity and good mechanical strength [96]. One of its key advantages is the absence of support structures, as the unsintered powder provides self-support during printing, making it particularly suitable for producing geometries with internal voids or overhangs [36]. However, SLS typically operates at high temperatures, which limits its use with temperature-sensitive biomolecules or living cells. Moreover, the resolution is constrained by laser spot size and powder grain size, making it less suitable for replicating microscale features.

4.2.3 Ink-jet printing

Among the powder-based additive manufacturing methods, inkjet printing relies on the precise deposition of liquid droplets onto a powder bed to selectively solidify the material. As illustrated in Figure 4.4, a thin layer of polymer powder is first spread across the build platform by a roller. A print head then selectively deposits a liquid binder onto specific regions of the layer that causes local solidification by either physical adhesion or chemical reaction. After each layer, the process repeats with the spreading of new powder and further binder deposition until the entire construct is formed.

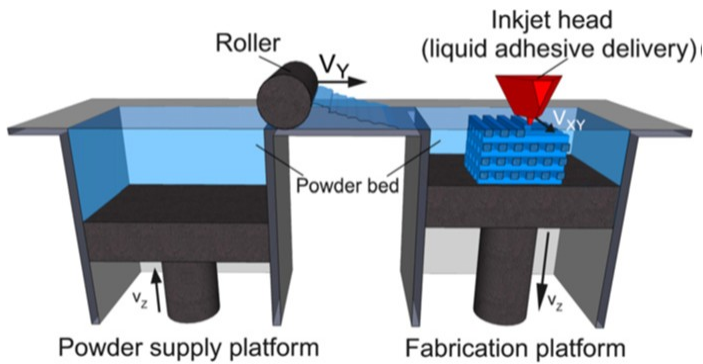


Fig. 4.4 Schematic of the Ink-jet process in which a roller spreads a thin layer of polymer powder over the previous layer, followed by selective solidification through the controlled deposition of a liquid binder, taken from [98].

Inkjet printing enables the fabrication of complex geometries with rel-

atively high resolution and design flexibility. Because the process operates at room temperature, it is particularly well suited for incorporating temperature-sensitive compounds. Moreover, localized binder deposition enables the incorporation of functional additives, such as bioactive molecules, or the direct combination of multiple material chemistries within the binder phase [36]. However, the process is limited by the narrow range of binder viscosities that can be reliably jetted and printed parts typically require post-processing to gain mechanical strength. These additional steps may reduce dimensional fidelity and affect the final resolution of the scaffold [96].

4.2.4 Fused deposition modeling (FDM)

Fused deposition modeling (FDM), also referred to as fused filament fabrication (FFF), is the most widely adopted extrusion-based additive manufacturing technique in the field of biomedical scaffold fabrication. As shown in Figure 4.5, a continuous filament of thermoplastic polymer is fed into a heated nozzle, melted and then extruded onto a build platform, following a predefined toolpath derived from a digital 3D model. Each extruded line cools and solidifies rapidly, bonding to adjacent and underlying layers to form a coherent three-dimensional structure.

The success of FDM in biomedical applications is largely attributed to its practicality, reproducibility and material compatibility. Biodegradable and biocompatible polymers such as PLA, PCL and poly(lactic-co-glycolic acid) (PLGA) can be readily processed in filament form and the method allows for the generation of scaffolds with well-defined, interconnected macropores [96]. The extrusion process enables the formation of highly regular internal architectures with consistent porosity across the construct, which contributes to both biological functionality and mechanical integrity [36, 96]. Furthermore, FDM has proven particularly effective for producing grid-like or lattice scaffold designs, which are commonly used to promote cell migration and guide tissue regeneration [100].

One of the main advantages of FDM lies in the possibility of customizing the filament composition before printing. Through melt-compounding, functional fillers such as bioactive ceramics, drugs, growth factors or plasticizers can be embedded into the polymer matrix, yielding filaments with tailored biological and mechanical properties [36]. This allows therapeutic agents to be integrated directly into the scaffold during fabrication, without

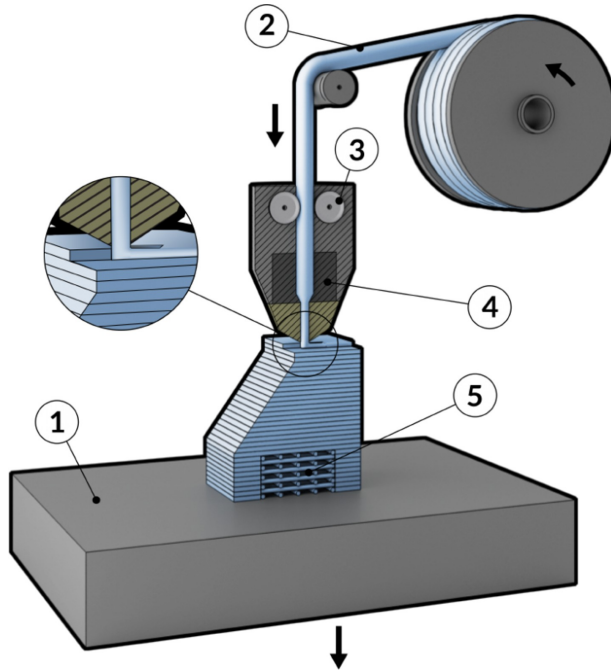


Fig. 4.5 Schematic of the FDM process where the object is built on a mobile platform (1). The polymer filament (2) is pulled by rollers (3) into a heated nozzle (4) and the molten polymers are printed layer-by-layer to build the final object (5), taken from [99].

requiring post-processing. Compared to techniques using photopolymers or powder beds, FDM provides greater robustness in handling complex material formulations and ensures good distribution of additives throughout the construct [101]. Moreover, because filament fabrication can be performed in-house, researchers can adjust polymer blends and additive loading ratios to suit specific biomedical applications. Combined with the widespread availability of open-source software and desktop-scale printers, these features make FDM an accessible and flexible platform for both academic research and early-stage clinical prototyping [96, 100].

However, the resolution of FDM remains limited by the nozzle diameter and the viscous behavior of the molten polymer, typically restricting feature sizes to the sub-millimeter range. Fine microscale porosity and surface smoothness are more difficult to achieve compared to light-based techniques such as stereolithography. In addition, the high extrusion temperatures

required for polymer melting are incompatible with most biological agents, making FDM unsuitable for direct printing of cell-laden constructs or thermosensitive compounds. Thermal degradation of sensitive molecules is a significant concern and post-processing steps are rarely sufficient to recover biological activity once compromised [101]. Nonetheless, due to its reliability, compositional flexibility, and ability to generate reproducible macroporous architectures, FDM remains one of the most practical and scalable techniques for engineering scaffolds in regenerative medicine.

4.2.5 Bioprinting

Bioprinting refers to a class of additive manufacturing techniques specifically adapted for the spatial deposition of bioinks, typically hydrogels laden with living cells, growth factors or other biologically active components. While it relies on principles similar to previously described methods, such as extrusion, inkjet or laser-assisted printing, these techniques are modified to operate under mild conditions compatible with the physicochemical and biological constraints of bioinks. Among them, the most commonly used one in tissue engineering is extrusion bioprinting, which follows a working principle similar to FDM. Instead of thermoplastic filaments, bioprinting employs viscous hydrogel solutions that are extruded through a nozzle at low temperature, often using pneumatic or mechanical pressure. The material is deposited layer-by-layer and solidification is achieved through physical gelation, ionic crosslinking or photopolymerization [36].

One of the main advantages of bioprinting is its ability to integrate living cells directly during fabrication, enabling the creation of cell-laden constructs with defined geometry and spatial organization. The low-temperature processing conditions preserve cell viability and the bioactivity of sensitive molecules, unlike thermoplastic-based methods such as FDM. However, bioprinting also faces significant technical challenges. Hydrogel-based materials typically exhibit low mechanical strength, limiting the structural integrity of printed constructs, especially in larger volumes. Achieving both shape fidelity and cell viability requires careful optimization of rheological properties and crosslinking kinetics. Moreover, maintaining homogeneity in cell distribution and preventing nozzle clogging are ongoing concerns. While current research continues to improve bioink formulations and printing strategies, bioprinting remains better suited for soft, low-load-bearing tissues, unless reinforced with additional structural components [96].

4.3 Additive manufacturing of PLA

PLA has become one of the most extensively studied and utilized materials in extrusion-based additive manufacturing [101, 102]. Its popularity stems not only from its biocompatibility and biodegradability but also from its ease of processing, particularly with FDM. Though often considered a straightforward material to print, PLA's final properties are highly sensitive to the specific conditions under which it is processed. A growing body of research has shed light on how adjustments can be made in printing parameters, thermal treatments and material formulations can dramatically alter the mechanical performance of printed parts.

4.3.1 Manufacturing parameters and interlayer cohesion

One of the most critical challenges in PLA printing lies in ensuring strong interlayer bonding. Poor cohesion between deposited layers is frequently identified as the primary source of mechanical weakness [101, 102, 103, 104]. In particular, samples printed in upright (layers are stacked perpendicular to the direction of applied load) orientations tend to fail along interfacial planes, while those printed on-edge (layers are deposited parallel to the applied load) or flat show significantly better tensile and flexural strength due to improved alignment with the direction of applied load. Experimental studies consistently demonstrate that reducing layer thickness and optimizing the orientation relative to loading directions significantly enhances mechanical performance [105, 106].

These mechanical trends have been corroborated by microstructural analyses. Using micro-computed tomography, von Windheim et al. [103] provided direct visual evidence of internal defects within printed PLA parts, as shown in Figure 4.6. Their 3D reconstructions revealed numerous voids located precisely between layers, with color-coded segmentation used to differentiate connected from isolated pores. Samples printed at high speeds or in YZ orientation displayed large continuous pores, indicative of insufficient fusion between deposited strands. These results underscore that, even when the external geometry appears intact, the internal structure of printed PLA often contains a high density of interfacial defects, which fundamentally compromise its mechanical reliability.

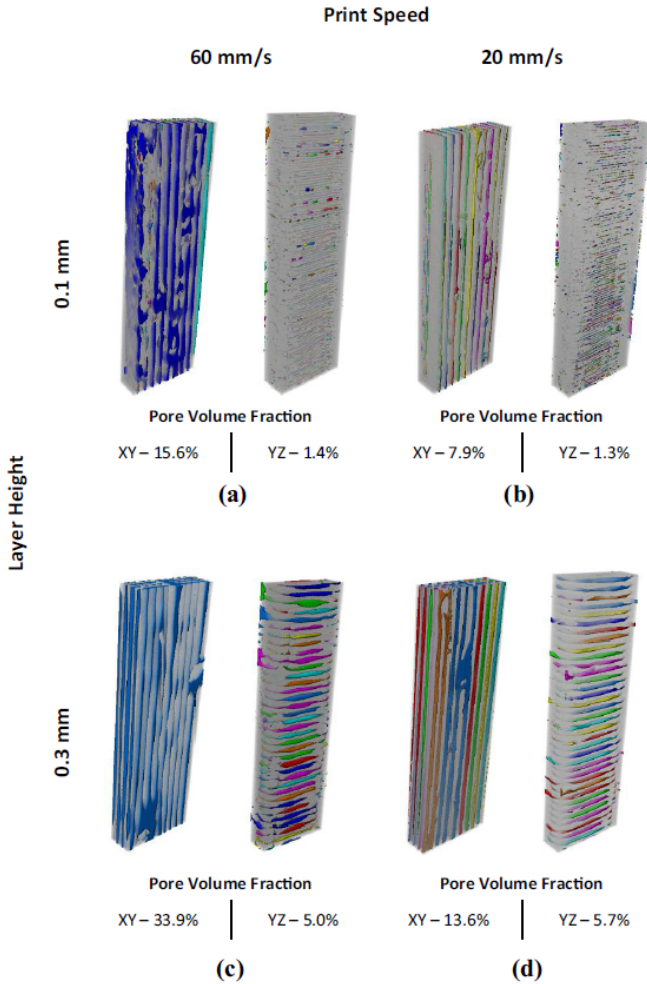


Fig. 4.6 Micro-CT image showing the interlayer porosity in PLA dogbone samples printed at different speeds. The colored regions correspond to connected pore volumes: pores sharing the same color are connected, whereas different colors indicate disconnected pores, taken from [103].

Low-temperature post-processing, such as annealing below T_g of PLA, has been shown to enhance interlayer adhesion by allowing PLA chain to partially diffuse across interfaces, reducing interfacial defects and improving tensile strength [103]. Increasing the build plate temperature during printing also promotes better fusion across layers [107].

SEM and micro-CT analyses reveal that the print quality and internal structure are also heavily influenced by extrusion speed and feed rate. When extrusion is too fast, incomplete bonding and internal voids form, compromising the structural integrity of the part. Optimal printing speed and nozzle temperature promote consistent layer deposition and stronger welds, confirming the critical balance between those two parameters [104, 108].

4.3.2 Crystallinity and post-processing

Although PLA is semi-crystalline by nature, the rapid cooling during FDM typically results in amorphous prints. However, crystallinity can be modulated post-process through annealing or controlled printing environments. For instance, thermal treatments at 80°C can increase crystallinity up to 40-45%, improving thermal resistance and dimensional stability without severely compromising ductility [103, 109].

The relationship between crystallinity and mechanical strength, however, is not straightforward. In several cases, increased crystallinity did not correlate with improved mechanical properties, particularly when the crystalline regions remained confined within individual filaments without bridging interfacial boundaries [103, 104]. Conversely, when crystallization occurs at the interface, as observed during printing with high build plate temperatures, it can positively contribute to mechanical reinforcement [107].

Overall, print-induced crystallinity tends to remain below 20% under standard conditions and its effect is often secondary to interfacial quality. Nonetheless, in applications requiring thermal resistance or long-term dimensional stability, the control over crystallinity remains a valuable tool.

4.3.3 Mechanical performance and anisotropy

The anisotropic nature of 3D printed objects produced via FDM is well established, and PLA is no exception. Differences in strength between orientations can exceed a factor of four. For instance, Chacón et al. [105]

reported tensile strengths ranging from approximately 20 MPa in upright configurations to 89 MPa in flat or on-edge orientations, depending on layer thickness and feed rate. This strong directional dependence is clearly illustrated in their Figure 4.7, which compares the stress–strain curves for the three build orientations. The upright samples exhibit brittle fracture with low elongation and early failure, while the flat and on-edge samples show higher strength and ductility, reflecting more effective load transmission along the printed filaments. Similarly, Luzanin et al. [104] and Abeykoon and coworkers [108] found optimized configurations achieving up to 65.8 MPa and 62 MPa under optimized parameter, respectively. SEM imaging shows that favorable orientations lead to ductile fracture modes, while upright-printed parts fail abruptly at layer interfaces [105].

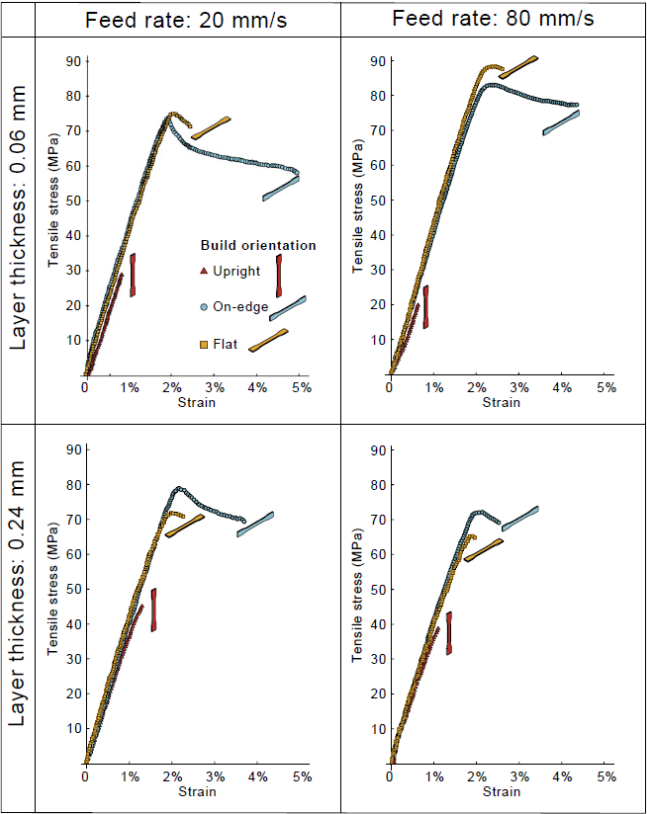


Fig. 4.7 Stress–strain curves of PLA specimens printed in three different build orientations (upright, flat, and on-edge), taken from [105].

These variations are primarily driven by the layered architecture of FDM and the quality of interfacial bonding. The thickness of each deposited layer influences the cross-sectional geometry of filaments, which in turn affects how well adjacent lines fuse together. Poor fusion results in stress concentrations and premature failure. Yao et al. [106] developed a strength model based on stress invariants for transversely isotropic materials, which accurately captures the effects of interlayer orientation and thickness on failure behavior. Their approach provides a predictive framework for optimizing print orientation to mitigate anisotropy and enhance structural reliability.

Interestingly, with carefully chosen parameters, FDM-printed PLA can match or even surpass the performance of injection-molded counterparts. This is especially true for impact strength, where enhanced interfacial crystallization and reduced void content lead to superior energy absorption capacity [107].

4.3.4 Formulation and functionalization

Beyond processing adjustments, modifying the composition of PLA filaments expands its functionality. The possibility of custom-compounding filaments with ceramic fillers, short fibers or plasticizers allows for property tuning tailored to specific applications. Studies have explored the incorporation of carbon fibers, hydroxyapatite, graphene, and other additives to enhance stiffness, bioactivity, or thermal performance [101, 102].

These strategies can be particularly useful when PLA is intended for structural applications or exposed to demanding environments. However, challenges remain in achieving homogeneous dispersion of additives and maintaining printability. In some cases, poor filler-polymer compatibility has led to interfacial porosity or nozzle clogging [101].

4.4 Creating hierarchical porosity

In the previous sections, microporosity and macroporosity were explored as distinct aspects of scaffold design. However, in many advanced biomedical applications, the most effective architectures for scaffolds are those that combine both micro- and macropores within the same structure. This

hierarchical porosity, where macropores promote cell migration and vascularization while micropores enhance surface area and support metabolic exchange, is increasingly seen as essential for biomimetic scaffold performance.

In most cases, macroporosity is directly induced into the object's geometry via 3D printing. Techniques like FDM offer precise control over filament path and spacing, allowing the creation of large, interconnected channels that replicate the size and distribution of natural tissue voids. However, microporosity is too small to be achieved by 3D printing and additional strategies must be employed to introduce it at the sub-filament scale. Over the past years, several approaches have been developed to address this need, each with its own mechanisms and constraints.

Among the most straightforward methods is particulate leaching. In a study by Shabab et al. [110], NaCl particles were blended with molten PCL before extrusion. The resulting filaments, printed in a conventional FDM setup, were then immersed in deionized water, where the salt slowly dissolved over 48 hours. The outcome was a scaffold that preserved its printed macroporous shape, but whose filaments contained homogeneously distributed micropores, as clearly visible in the SEM images of Figure 4.8. These micropores, typically below 50 μm , significantly increased the scaffold's surface area and improved the adhesion of osteoblast-like cells.

A similar approach was adopted by Gomez-Cerezo et al. [111], who incorporated phosphate-buffered saline (PBS) particles within a composite of PCL. Instead of water, they used a dilute NaOH solution as the leaching medium. This not only dissolved the PBS particles but also induced a controlled surface mineralization, leading to scaffolds with active phosphate and calcium surfaces. In both cases, particulate leaching proved to be a reliable route to microporosity, with the added benefit of preserving the mechanical integrity of the printed structure. However, the process depends on effective porogen removal, which can be time-consuming and may risk structural deformation if not carefully managed.

Rather than relying on porogen removal, some strategies introduce microporosity through physical foaming techniques such as CO₂ expansion. In this approach, the printed scaffold undergoes a post-processing step where gas is diffused into the polymer matrix under pressure, then rapidly released to trigger pore formation. This was demonstrated by Zhou et al. [113], who exposed pre-printed PLA structures to CO₂ at 5 MPa for 24 hours,

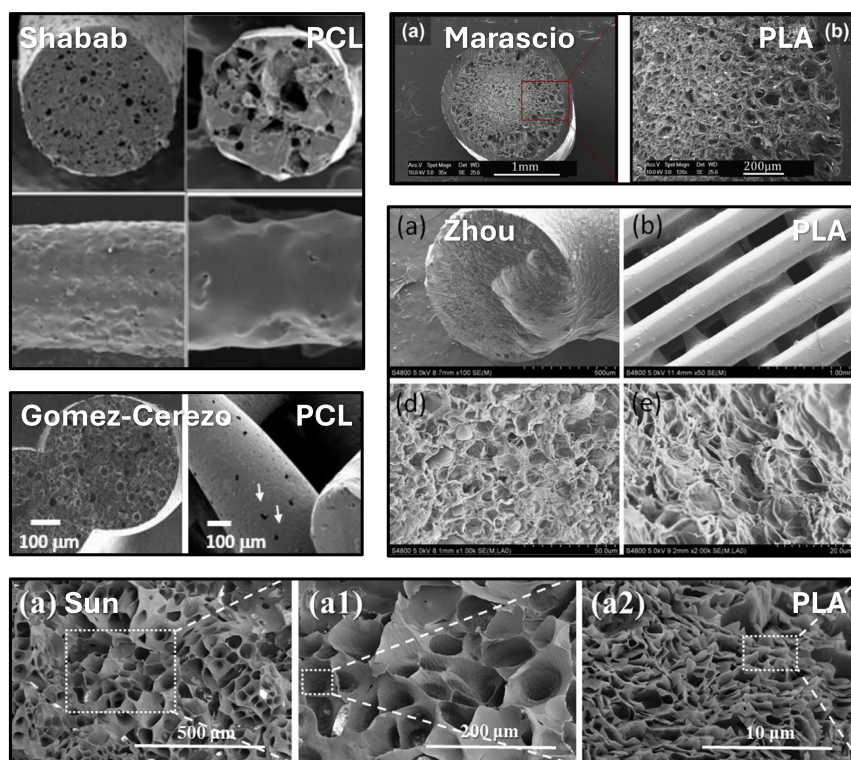


Fig. 4.8 Hierarchical porosities obtained by combination of 3D printing and particulate leaching (Shabab [110], Gomez-Cerezo [111]) using PCL, gas foaming (Marascio [112], Zhou [113]) and liquid-liquid phase separation (Sun [114]), using PLA.

followed by depressurization. The resulting microporosity shown in Figure 4.8, typically in the 1–10 μm range, was evenly distributed across the filament cross-sections. Notably, the process preserved the macro-architecture defined by 3D printing, while introducing a finer porosity within.

Building on this idea, Marascio et al. [112] developed a more integrated strategy by saturating PLA filaments with CO₂ before printing. During the extrusion step, the sudden drop in pressure and rise in temperature caused the gas to expand in real time, creating microporosity directly during filament deposition. This in situ foaming approach offers two major advantages: it eliminates the need for post-processing and allows for localized control of porosity by adjusting print parameters. At lower extrusion

temperatures, a dense skin formed on the filament surface, encapsulating a porous core as shown on Figure 4.8. At higher temperatures, pore distribution became more homogeneous across the cross-section.

A third route to hierarchical porosity involves liquid–liquid phase separation. In contrast to the previously discussed techniques, no 3D printing is involved here, both the macro- and microporosity emerge spontaneously during solvent evaporation. In the work of Sun et al.[114], PLLA was dissolved in chloroform and mixed with ethanol as a non-solvent to trigger phase separation. As the solvent slowly evaporated, the system segregated into polymer-rich and solvent-rich regions, with the former progressively solidifying into a porous matrix. The resulting morphology was highly dependent on the initial polymer concentration. At low concentrations, the separation was rapid and led to the formation of fibrous, sponge-like networks as shown in Figure 4.8. At intermediate levels, spherical, hollow microstructures appeared. At high concentrations, a hybrid morphology combining both was observed. This approach enables the formation of both micro- and macroscale porosity within a single fabrication step. However, the use of organic solvents and long drying times may limit its practical integration with standard additive manufacturing processes.

Together, these strategies highlight the range of techniques available to introduce microporosity, each with its own strengths and trade-offs. Particulate leaching offers simplicity and compatibility with standard printing but requires long post-processing steps. Gas foaming avoids solvents and allows for clean integration, yet demands precise control over pressure and temperature. Phase separation, while solvent-dependent, enables fine tuning of pore morphology through simple formulation parameters. However, in this latter case, the final shape of the object cannot be precisely controlled but it nevertheless demonstrates that hierarchical porosity can be achieved without complex tooling. The images presented in Figure 4.8 allow for a direct comparison of the different morphologies obtained with each method and clearly highlight the diversity of pore architectures that can be achieved.

4.5 Porosity induced in PLA/PEG blends

4.5.1 Microporosity in PLA/PEG blends

The formation of microporosity in PLA/PEG blends emerges predominantly from phase separation phenomena combined with selective removal of PEG. Among the most widely used strategies, solvent casting followed by extraction offers a simple yet powerful route to generate porous networks. Across studies adopting this technique [115, 116, 117], a common observation is that PEG, especially at contents above 20%—leads to the formation of distinct microdomains that, once leached, result in interconnected pores on the order of 1–10 μm . However, the precise morphology and connectivity of these pores remain highly dependent on processing parameters.

For instance, in the work of Huang et al. [115], a blend of PLA and PEG was cast with salt particles and subjected to solvent evaporation, followed by particulate leaching. The resulting scaffolds combined larger pores (250 μm), templated by salt crystals, with a secondary microporous (5 μm) structure arising from PEG extraction as shown in Figure 4.9. Notably, the presence of "cave-like" features was evident only in blends containing 20–30% PEG, confirming that above a critical PEG threshold, phase separation becomes sufficiently coarse to yield a defined microporosity.

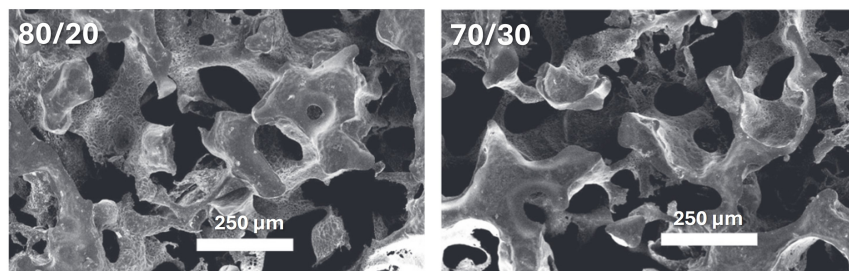


Fig. 4.9 SEM images of microporosity obtained by solvent casting of PLA/PEG 80/20 (left) and 70/30 (right) blends combined with NaCl leaching, adapted from [115]. The scale bars are of 250 μm .

A comparable mechanism underlies the porous morphologies reported by Lai et al. [117], although the porosity in this case is shaped by thermal crystallization control rather than salt leaching. Their approach involved

blending PLA with PEG and subjecting the cast films to controlled crystallization at either 100°C or 130°C before PEG extraction. Higher crystallization temperatures induced greater exclusion of PEG from the crystalline PLA phase, producing more open, fibrillar micropores ranging from 150 nm to over 1 μm , as shown on Figure 4.10. Importantly, this method enabled precise tuning of pore dimensions without the use of porogens, thereby avoiding the irregularities often associated with leaching processes.

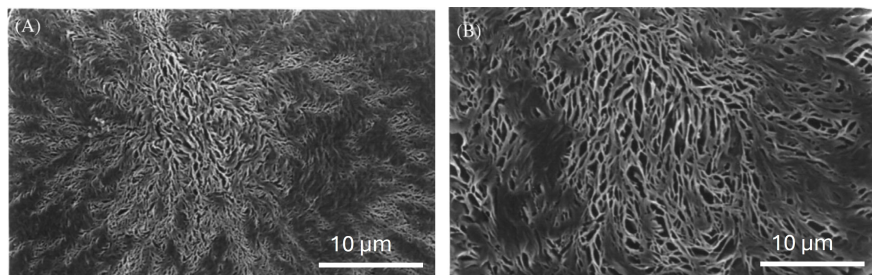


Fig. 4.10 SEM images of microporosity obtained by PEG extraction after crystallization of the PLA/PEG 50/50 blend at 100°C (A) and 130°C (B), adapted from [117].

The formation of microporosity via electrospinning represents a third strategy, which combines polymer phase separation with rapid solvent evaporation under controlled humidity. In the study by Wang et al. [118], PLA/PEG nanofibers loaded with curcumin exhibited surface microporosity whose size and distribution varied with PEG content and spinning conditions. Fibers obtained with lower amount of PEG ($\pm 10\%$) exhibited clear surface porosity, with micron-sized cavities directly visible on the fiber walls, as shown on Figure 4.11. These surface pores are attributed to the migration of PEG to the fiber surface followed by solvent evaporation and PEG leaching. In contrast, higher PEG contents (between 50 to 75%) led to smoother, non-porous fiber surfaces. However, no explanation is provided as to why phase separation does not occur with higher PEG content. Although the microporosity was confined to the fiber surface, the overall porosity, measured by capillary flow porometry, is typically between 1-4 μm in diameter, depending on the PLA/PEG ratio.

Although most PLA/PEG systems rely on PEG extraction to generate microporosity, certain block copolymer architectures can also lead to porous

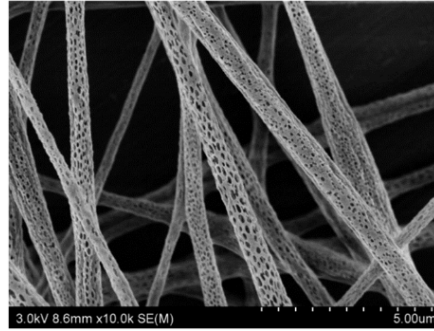


Fig. 4.11 SEM images of electrospun fibers made of PLA/PEG 90/10 blend, taken from [118].

structures without any selective removal step. In the study by Lins et al. [42], PLA-PEG-PLA triblock copolymers processed via electrospinning yielded fibrous mats exhibiting surface microporosity. In this case, the PEG segments remain covalently bound within the macromolecular structure and are not extracted.

While the PEG remains integrated within the polymer structure in this system, a secondary level of porosity could theoretically be introduced by selectively removing the PEG domains through chemical etching. However, such an approach would compromise the structural cohesion of the material, as the copolymer relies on the integrity of both blocks for mechanical stability. In addition, unlike the simple aqueous extraction used in PLA/PEG blends, the cleavage of covalently bound PEG segments in block copolymers would require the use of specific chemical reagents, with a risk of leaving residual by-products within the scaffold.

4.5.2 Macroporosity and 3D printing of PLA/PEG blends

Unlike microporosity, which arises intrinsically from the material's thermodynamics, macroporosity must be externally imposed through architectural design. 3D printing and other additive manufacturing techniques enable the direct creation of macroporous scaffolds by modulating filament layout, strand spacing and print path. Within this framework, PLA/PEG blends offer not only improved printability due to the plasticizing effect of PEG, but also introduce processing-induced morphological variations that influence

the final scaffold architecture.

Serra et al. [13] demonstrated how PEG content directly affects the geometry of printed PLA/PEG scaffolds. At 5% PEG, the printed filaments were well defined, yielding regular pores of predictable size. Increasing the PEG content to 20% led to broader struts, rounded pore shapes and a drop in overall porosity. These changes were attributed to the reduction in melt viscosity caused by PEG, which increased filament spreading during extrusion and reduced the sharpness of pore boundaries. A similar balance was observed by Salehi et al. [90], who systematically evaluated PLA/PEG blends printed with PEG concentrations from 5% to 20%. Their results confirmed that low PEG levels preserved macropore architecture, while higher contents distorted macropore shapes.

Even in studies where macroporosity was not the primary focus, such as Gao et al. [119] and Kumar et al. [120], the role of PEG in modulating inter-filament bonding and intrinsic voids is well documented. Gao et al. showed that the incorporation of PEG with different molar masses significantly altered neck formation between printed filaments. PEG of intermediate molar mass (8000 g/mol) achieved the best interlayer adhesion and minimized inter-filament voids, while high- M_w PEG (20000 g/mol) led to void enlargement due to poor diffusion dynamics. Kumar et al. [120], using PLA/PEG blends with 1–5% PEG, reported a decrease in brittleness, as evidenced by higher elongation at break and impact strength. SEM images of the fracture surfaces showed smoother and more continuous morphologies compared to neat PLA, reflecting the increased ductility imparted by PEG.

Although these results do not directly address macroporosity, they provide critical insights into the printability and interfacial behavior of PLA/PEG filaments during 3D printing. This knowledge is essential, as it is precisely the 3D printing process that enables the introduction of controlled macroporosity into PLA/PEG materials.

4.5.3 Toward hierarchical porosity in PLA/PEG materials

The combination of these micro- and macro-structural phenomena naturally points toward the possibility of generating hierarchically porous PLA/PEG scaffolds. While few studies explicitly target this objective, works such as those by Serra et al. [13] and Salehi et al. [90] indicate that increasing

PEG content not only affects macropore geometry but also enhances surface roughness and local complexity at the pore wall. In parallel, Lai et al. [117] demonstrated that thermal control of crystallization in PLA/PEG blends enables the formation of finely tuned microporous networks, even without the use of porogens. Although this approach has not yet been integrated with 3D printing, it points to a promising direction where intrinsic material processes, such as phase separation or crystallization, can be used to create microporosity, while 3D printing provides the macroscopic geometry.

5

Limitations of the current literature and research gaps

Despite substantial progress in understanding the crystallization behavior of PLA and its blends with PEG, persistent research gaps continue to hinder the development of systematic strategies for engineering hierarchically porous architectures via additive manufacturing. These limitations concern both the fundamental understanding of phase behavior and the practical control of multi-scale porosity during processing.

Incomplete understanding of phase behavior Many studies refer to the phase behavior of PLA/PEG blends in terms of partial or limited miscibility. However, phase diagrams are often theoretical or derived from indirect indicators, and few have been experimentally validated across composition, molar mass and temperature. Techniques such as dual T_g detection or melting temperature depression are commonly used to infer miscibility, yet these methods show limited reliability in PLA/PEG systems, especially due to overlapping transitions and complications induced by crystallization and reorganization upon heating. As a result, the true miscibility window and phase boundary conditions remain poorly defined.

Unclear localization of PEG during PLA crystallization Although several hypotheses have been proposed regarding the post-crystallization distri-

bution of PEG, including homogeneous dispersion within the amorphous PLA phase or segregation at spherulite boundaries, the literature lacks systematic morphological evidence to confirm these mechanisms. This reflects a more general lack of studies that directly observe the interplay between phase separation kinetics and crystallization dynamics, which remains a key aspect for controlling pore morphology. Moreover, there is currently no predictive framework that correlates blend composition, crystallization dynamics and PEG spatial distribution with the resulting porous morphology after extraction.

Inadequacy of conventional DSC to study fast-crystallizing PEG The majority of studies rely on conventional DSC to characterize PLA/PEG blends. However, PEG is known to crystallize extremely rapidly during cooling, often before the onset of isothermal steps. This limits the accuracy of DSC-based interpretations, particularly regarding phase separation and PEG mobility. Despite this challenge, few works employ rapid thermal techniques such as flash DSC to overcome this limitation, resulting in a biased or incomplete view of crystallization behavior.

Absence of hierarchical porosity made of PLA/PEG blends in literature

While PLA/PEG blends are frequently used to generate micro-porosity through PEG extraction, and 3D printing is recognized for inducing macro-porosity, no existing study successfully integrates these two mechanisms into a coherent hierarchically porous system. The potential synergy between phase separation and additive manufacturing remains largely unexplored, leaving a significant gap in strategies for multiscale structural control using this blend.

PART II

Objectives and strategy

1

Objectives

PLA and PEG are two abundant, easily produced, and inexpensive materials. PLA is among the most widely used polymers in 3D printing, while PEG is well known for its plasticizing effect of PLA. Moreover, both materials are biocompatible. These characteristics make them particularly attractive for biomedical applications. Given the complexity of the human body and its functions, the requirements for materials suitable for such applications are substantial. In the case of scaffolds, it is not only essential for the materials to be biocompatible and possibly biodegradable, but also to possess appropriate mechanical properties and a tailored architecture, potentially tailored to the patient. A promising strategy would involve combining PLA and PEG with simple fabrication techniques to ultimately produce objects with both adequate properties and intricate structures. This would represent a significant advancement in the field of personalized medicine, which requires fast and straightforward methods suitable for on-site implementation, thus reducing response times in clinical interventions.

In this thesis, the strategy consists in combining PLA and PEG with additive manufacturing techniques to fabricate scaffolds that exhibit both the required mechanical properties and complex, customizable architectures after specific PEG extraction. However, fully exploiting this potential requires addressing several unresolved challenges. These include a deeper understanding of the phase diagram of PLA/PEG blends, the mechanisms driving phase separation and crystallization, and the conditions under

which hierarchical porosity can be reliably introduced and controlled. The objective of this thesis is therefore to develop a robust and versatile strategy for the fabrication of PLA/PEG-based scaffolds with hierarchical porosity and mechanical properties tailored to the demands of personalized biomedical applications.

First, it is necessary to understand the thermodynamic interactions and phase behavior of PLA/PEG blends. Although partial miscibility has been reported, the precise miscibility limits and phase separation pathways (liquid–liquid or liquid–solid) remain poorly defined and often inferred from indirect thermal indicators. An experimental phase diagram must be established to clarify the regimes of homogeneous mixing, phase separation in the blend and crystallization-induced segregation. Particular attention should be paid to the spatial distribution of PEG in the PLA matrix, as it directly determines the morphology of the porous network after PEG removal.

Second, the crystallization of PLA in the presence of PEG must be characterized with high precision. Beyond its role in phase separation and microstructural development, crystallization also governs the mechanical behavior of the material. The degree of crystallinity directly influences stiffness, ductility, and fracture resistance, making it a critical parameter for designing scaffolds with appropriate mechanical performance. Moreover, the presence of PEG alters the crystallization kinetics of PLA by increasing chain mobility but also modifies the morphology and crystalline organization. These effects are complex and strongly dependent on the PEG content, molar mass and processing conditions. To accurately evaluate these effects, it is essential to decouple the crystallization of PLA from that of PEG, which is known to crystallize extremely fast, although at lower temperatures, and potentially interfere with PLA ordering during conventional DSC analysis.

Third, the morphological consequences of phase separation and crystallization must be linked to the formation of porosity. In particular, the formation of microporosity through PEG extraction must be related to the localization of PEG within or around PLA spherulites. It is essential to determine under which conditions PEG remains trapped inside the crystalline domains, forms interconnecting amorphous regions or accumulates at the growth front of PLA lamellae. Such distinctions are key to predict and control the porous architecture at the microscale.

Finally, the integration of this material strategy with additive manufacturing techniques, especially fused deposition modeling (FDM), must be evaluated as a route to introduce macroporosity and obtain fully hierarchical scaffolds. Although various studies have independently addressed microporosity in PLA/PEG systems and macroporosity via 3D printing, no current study successfully combines both approaches in a consistent and reproducible way. Therefore, this thesis aims to demonstrate the feasibility of producing hierarchically porous PLA/PEG constructs by coupling phase separation with 3D printing, while maintaining mechanical integrity.

To summarize, the specific objectives of this thesis are:

1. To experimentally map the phase behavior of PLA/PEG blends as a function of composition, temperature and PEG molar mass.
2. To investigate the crystallization kinetics and morphology of PLA in blends with PEG.
3. To establish the relationship between crystallization-induced phase separation and the formation of microporosity through PEG extraction.
4. To evaluate the influence of blend formulation and processing conditions on the mechanical properties of the resulting materials.
5. To develop a combined strategy coupling PLA/PEG formulation and additive manufacturing to fabricate scaffolds with controlled hierarchical porosity.

2

Research strategy

To address the objectives outlined in this thesis, a multi-step experimental approach was developed to systematically explore the crystallization behavior, phase separation mechanisms and porous structure formation in PLA/PEG blends. The aim of this strategy is to establish a clear understanding of how thermal behavior and phase organization influence the morphology and performance of these materials, with the ultimate goal of fabricating hierarchically porous scaffolds through additive manufacturing using only accessible processing methods and simple materials. The research strategy was divided into five main stages, each targeting a specific scientific question and building upon the previous step. These five steps are summarized schematically in Figure 2.1 at the end of this section, which provides an overview of the experimental workflow developed in this thesis.

2.1 Understanding the crystallization of PLA and PEG

Before investigating complex blend systems, it is essential to establish baseline knowledge of the thermal and morphological behavior of the pure components. This step allows for the identification of characteristic crystallization temperatures, transition ranges and kinetic parameters for both

PLA and PEG, which serve as references in later analyses of mixtures.

Conventional differential scanning calorimetry (DSC) was used to determine the glass transition temperature (T_g), cold crystallization temperature (T_{cc}) and melting point (T_m) of each polymer under standard heating and cooling rates. Although conventional DSC is suitable for studying pure components, it does not offer sufficiently fast cooling rates. As will be explained in detail in the section regarding the phase diagram, it is imperative to quench the blend below the T_g of PEG without any crystallization occurring during the cooling phase in order to obtain a well-defined starting point for the following theoretical analysis. Therefore, flash DSC was used to determine the minimum cooling rate required to suppress PEG crystallization during quenching. Moreover, due to the high cooling and heating rates applied in fDSC, thermal transitions are kinetically controlled and may appear at different temperatures compared to those measured by conventional DSC. For this reason, both methods were employed: conventional DSC reflects more realistic thermal conditions achievable during processing, while fDSC provides the theoretical framework necessary for precise thermal control and phase diagram construction.

Additionally, polarized optical microscopy (POM) was used to observe the crystalline morphology of PLA. Particular attention was paid to the nucleation density, spherulite size, and radial growth rate as a function of crystallization temperature. These morphological features provide direct insights into the crystallization behavior of PLA and how it is influenced by thermal conditions, which in turn affects the final structure and mechanical properties of the material.

This foundational step established the thermal and morphological baselines of PLA and PEG, which are essential for interpreting the influence of one component on the other in blends. Without a clear reference, the specific effects of blending on crystallization and phase behavior cannot be reliably assessed.

2.2 Investigating the crystallization of PLA/PEG blends

Having defined the crystallization characteristics of the individual components, the next stage of the strategy focused on the thermal behavior of PLA/PEG blends. The same set of analytical techniques, i.e., conventional DSC and fDSC, was employed to investigate the blends, allowing for direct comparison with the results previously obtained for the pure polymers. This comparative approach made it possible to assess the influence of PEG on the crystallization behavior of PLA, as well as to detect possible crystallization of PEG itself within the blend. This analysis served a dual purpose. On one hand, the aim was to understand how PEG, acting as a plasticizer, affects PLA crystallization kinetics and overall crystallinity. On the other hand, the presence or absence of distinct melting and crystallization events for each component also serves as an indirect indicator of phase separation. If a component remains molecularly dispersed, its crystallization may be suppressed and no corresponding peak observed; conversely, the detection of thermal crystalline transitions suggests that phase separation occurred, forming domains large enough to crystallize independently.

To study these effects, PLA/PEG blends were prepared with varying PEG contents (10 wt%, 30 wt%, and 50 wt%) and different PEG molar masses (3000 g/mol (3K), 100 000 g/mol (100K) and 1 000 000 g/mol (1M)). These specific compositions were selected to represent a range of blend conditions: 10 wt% corresponds to a minor PEG content dispersed in a PLA-rich matrix, 30 wt% represents an intermediate formulation, which is also the most common boundary for phase separation reported in the literature and 50 wt% provides a balanced ratio between the two components and is situated well above the boundary of phase separation. Similarly, the chosen molar masses span three regimes: 3K is significantly lower than the molar mass of PLA used in this research and represents a short-chain plasticizer; 100K is roughly equivalent to the PLA molar mass and 1M is much higher.

X-ray diffraction (XRD) measurements were conducted to determine the crystalline structure of PLA in the presence of PEG. Particular attention was given to potential changes in the unit cell parameters, crystal form (α or α') and degree of crystallinity as a function of PEG content and molar mass. Beyond the structural analysis of PLA, XRD also enabled the quantification

of the crystalline fraction of PEG. By comparing the total PEG content to the amount detected in the crystalline phase, it was possible to estimate the proportion of PEG that remained amorphous and therefore likely dispersed within the amorphous domains of the blend.

The presence of PEG is expected to influence the radial growth rate and banding characteristics of PLA spherulites, depending on its content, molar mass and the thermal conditions applied. POM was therefore employed to monitor these morphological features and to assess how PEG affects the nucleation and growth environment of PLA crystals. In addition to characterizing the PLA crystalline morphology, POM was also used to investigate the possible formation of PEG-rich domains. If phase separation occurs and the PEG-rich regions grow to a size compatible with optical resolution, they may become visible under polarized light due to their birefringence or by contrast with surrounding phases.

2.3 Mapping the phase behavior of PLA/PEG blends

The previous analyses conducted by DSC, POM and XRD revealed indirect signs of phase separation, offering a first glimpse of the underlying phase diagram. However, these techniques remain too limited to accurately define phase boundaries or establish a complete and reliable phase diagram. To address this limitation, the next step of the strategy focused on constructing a comprehensive experimental phase diagram capable of capturing both thermal transitions and the mechanisms of phase separation, including liquid–liquid (LL) demixing and crystallization-induced liquid–solid (LS) segregation.

To achieve this, blends of PLA and PEG were subjected to precisely controlled thermal protocols using flash DSC (fDSC), which enables near-instantaneous temperature changes and minimizes structural rearrangements during cooling. The experimental strategy consisted of a two-step quenching process. First, the sample was rapidly heated to the molten state and quenched to a selected isothermal temperature, where it was held long enough to allow crystallization and/or phase separation to occur. Then, a second quench brought the sample to a very low temperature, below the glass transition of PEG, effectively freezing the microstructure in the

state it had reached during the isothermal step. During the subsequent fast heating scan, the thermal transitions observed for PLA and PEG provided indirect information about the phase state and crystallization behavior of each component at the isothermal holding temperature.

This method was systematically applied to blends containing three PEG molar masses (3K, 100K and 1M), three compositions (90/10, 70/30, and 50/50 PLA/PEG by weight) and using a range of isothermal temperatures from 200°C down to 50°C.

The goal of this approach was to construct an experimental phase diagram capable of delimiting regions of homogeneous mixing, LL phase separation and crystallization-induced LS segregation. By systematically varying PEG content, molar mass and isothermal temperature, the resulting thermal signatures could be categorized into distinct types of behavior, allowing for a qualitative mapping of phase transitions. Such a diagram would serve as a central tool for interpreting subsequent morphological and porosity data, and provide a predictive framework for selecting blend compositions and thermal treatments to achieve specific microstructural outcomes.

2.4 From phase separation to porosity and PEG localization

Once the crystallization and phase separation behavior had been mapped, the next step was to investigate how these phenomena affected the spatial distribution of PEG within the PLA matrix and the resulting porosity after PEG extraction.

PEG acts as a porogen in the system: it is miscible with PLA under certain conditions but can be selectively removed, at least partially, by water immersion due to its solubility. However, the morphology of the pores generated by this process depends on where and how PEG is distributed within the blend prior to extraction. After crystallization, PEG can be located either in the interspherulitic regions or within the intraspherulitic amorphous zones of the PLA matrix. Depending on the degree of phase separation, PEG may be totally dispersed or form PEG-rich domains of varying size. Upon selective extraction, these spatial distributions give rise

to distinct microporous morphologies, closely linked to the thermal history and crystallization pathway of the blend. These configurations may also coexist within the same material, depending on the crystallization kinetics and phase behavior.

To explore these scenarios, selected PLA/PEG blends were thermally treated to impose specific crystallization regimes and then subjected to PEG extraction in water. The efficiency of PEG extraction can be assessed by proton nuclear magnetic resonance spectroscopy (NMR), which enables quantification of any residual PEG in the material. The absence or near-complete disappearance of PEG signals would indicate that the extraction solvent was able to access the entire PEG-rich phase, thereby suggesting a continuous and interconnected porous network.

The morphology of the resulting porous structures was first examined by scanning electron microscopy (SEM). Both surface and cross-sectional observations were performed to determine whether the porosity extended throughout the bulk material or was limited to the outer regions. The presence of internal pores, visible in fractured or sectioned samples, would further support the hypothesis of an interconnected PEG phase prior to extraction.

In addition to SEM, micro-computed tomography (micro-CT) was employed to visualize the three-dimensional structure of the samples without the need for physical sectioning. This non-destructive technique not only confirmed the presence of volumetric porosity but also enabled the quantification of the total pore volume across the entire sample. As such, it provided a complementary dataset to assess the spatial distribution and connectivity of the porous network.

Together, these methods were intended to correlate the thermal history and predicted phase behavior of the blends with the resulting microporous architecture and to determine under which conditions interconnected porosity could be reliably obtained through PEG extraction.

2.5 Achieving hierarchical porosity via 3D printing

The final stage of the research strategy aimed to translate the insights gained from the previous experiments into a scalable process for fabricating scaffolds with hierarchical porosity. While microporosity can be generated through PEG extraction, macroporosity had to be introduced through structural design — and 3D printing was chosen as the enabling technology.

Before 3D printing can be performed, PLA/PEG blends must first be processed into filaments compatible with fused deposition modeling (FDM). This requires careful optimization of the extrusion parameters to ensure the production of homogeneous, defect-free filaments, as any material heterogeneity may compromise printability and structural consistency. Once reliable filaments are obtained, they will be used to fabricate 3D objects in order to assess the feasibility of combining macroporosity — introduced through 3D printing — with microporosity generated by PEG extraction. At this stage, the aim is not to optimize the macroporous architecture but rather to demonstrate the integration of both porosity scales within a single construct. A gyroid design was selected due to its isotropic geometry and regularity, which facilitate a clear evaluation of hierarchical porosity.

In order to evaluate the mechanical properties of the developed materials, uniaxial tensile tests are conducted on a range of reference and processed samples. The goal is to compare the influence of processing method, porosity, crystallinity and PEG content on tensile performance. Tested specimens include commercial PLA filaments, injection-molded PLA, 3D-printed PLA and PLA/PEG blends under controlled conditions. The effect of macroporosity is assessed by varying the pore size within printed structures, while the impact of crystallinity is investigated through annealing treatments. Additionally, PLA/PEG blends and their extracted forms are included to quantify the mechanical consequences of PEG incorporation and micropore formation. This comparative strategy is intended to identify the key factors governing mechanical performance in relation to hierarchical porosity and thermal history.

This final stage brings the strategic approach of this thesis to an end, bridging the gap between the fundamental understanding of phase behav-

ior and the practical realization of a functional material system. Through this work, the interactions between PLA, PEG and processing conditions are clarified, enabling the fabrication of complex hierarchically porous structures using only simple materials and accessible methods. To help visualize the overall research approach, Figure 2.1 summarizes the methodological workflow and the corresponding characterization methods.

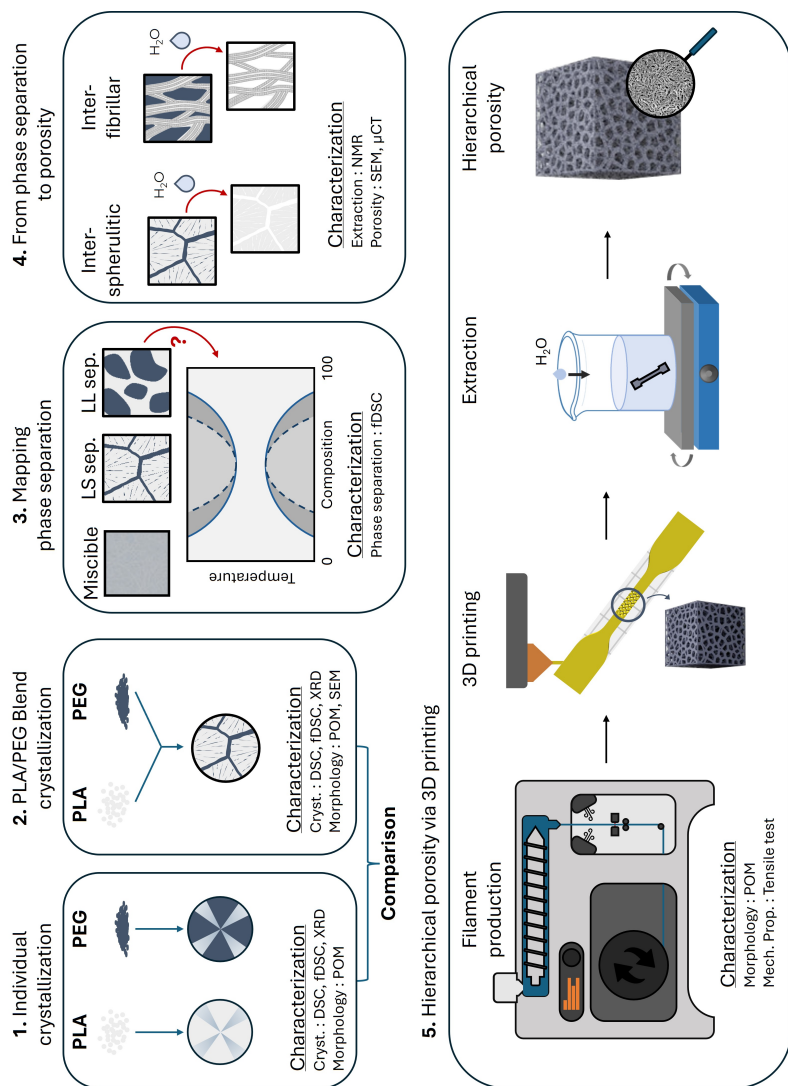


Fig. 2.1 Schematic overview of the experimental strategy developed in this thesis to design hierarchically porous PLA/PEG structures. The workflow begins with the separate characterization of PLA and PEG crystallization behaviors (1.), followed by the study of crystallization in their blends (2.). Phase separation is then mapped as a function of composition and temperature using flash DSC (3.), serving as a basis to understand how porosity emerges upon PEG extraction (4.). The final step involves the translation of these insights into a 3D printing-based process to fabricate objects with controlled hierarchical porosity (5.).

PART III

Methodology

Materials and Methods

1.1 Materials

The poly(L-lactic acid) (PLA) used in this work was pellets of Ingeo 2500HP from NatureWorks. Its weight-average molar mass (M_w) is reported to be around 10^5 g/mol with a dispersity of 1.7 and the D-lactide content is less than 0.5%. Poly(ethylene glycol) (PEG) powders with a M_w of 3350 g/mol (PEG 3K), 100 000 g/mol (PEG 100K) and 1 000 000 g/mol (PEG 1M) were purchased from Sigma-Aldrich. Chloroform (CHCl_3) and deuterated chloroform (CDCl_3) were also purchased from Sigma-Aldrich and used as received. The commercial PLA filament (cPLA) used for 3D-printing was EasyFil PLA (Blue) purchased from Form Futura.

1.2 Sample preparation

1.2.1 Production of PLA/PEG films by solvent casting

PLA pellets and PEG powder were dried overnight at 40°C under vacuum before processing. PLA/PEG blends with different compositions (10, 30

and 50 PEG wt. %) were dissolved in CHCl_3 to obtain a total polymer concentration of 40 mg/mL. The vials were then hermetically closed to prevent evaporation of the solvent. The solutions were magnetically stirred until the obtention of a homogenous transparent liquid and further cast on glass Petri dishes. The solvent was removed by evaporation overnight at room temperature. The thickness of the films was measured with a micrometer and was around 100 μm .

This solution-casting method was not only employed to produce thin films but also to ensure a homogeneous composition of the PLA/PEG blend. Consequently, most of the samples used for subsequent characterizations were prepared using this protocol and later reshaped as needed to meet the specific requirements of each characterization technique. Throughout this thesis, the blends are named after the PEG molar mass and the composition. Therefore, PLA/PEG100K 70/30 corresponds to the blend made of PLA HP2500 at 70 % wt. and PEG100K at 30 % wt.

1.2.2 Crystallization of PLA/PEG films using hot pressing method

Before use, PLA/PEG films were dried overnight at 40°C under vacuum. Dried films were then sandwiched between two metallic plates covered by Kapton foils. A 100 μm thick aluminum foil was cut and used as mold to obtain samples of 5 mm x 5 mm. To eliminate the thermal history, these blend assemblies were first put in a hot press at 200°C for 5 min, then transferred to a second hot press at 110°C and let crystallize for 4h. Minimal pressure was applied to allow a good contact on both faces of the samples. At the end, PLA/PEG films were quenched in air from 110°C to room temperature.

1.2.3 Production of PLA/PEG filament for 3D-printing

First of all, PLA pellets and PEG100K powder were mixed in a 70/30 wt.% ratio and dried under vacuum at 50°C for 24h before use. Drying was necessary to eliminate residual moisture and ensure processing stability.

The filament production was carried out in two complementary steps to ensure both compositional homogeneity and diameter consistency. The first step involved preparing a homogeneous PLA/PEG blend by feeding a mixture of PLA pellets and PEG powder into a twin-screw extruder. This

process allowed for efficient mixing and the resulting extruded filament was compositionally uniform but displayed significant diameter irregularities. To address this, the extruded filament was pelletized to obtain PLA/PEG pellets. These pellets were then processed in a single-screw extruder specifically designed to produce filaments with a constant diameter of 1.75 mm, needed for 3D printing. This two-step approach was essential: while the twin-screw extrusion ensured compositional uniformity through effective mixing and longer residence time, it lacked control over filament diameter. Conversely, the single-screw extrusion provided precise diameter control but was insufficient to achieve proper mixing due to shorter residence times and limited shear.

1.2.3.1 First extrusion

To ensure a homogeneous blend, PLA pellets and PEG powder were first processed using a Thermo Scientific Process 11 parallel twin-screw extruder equipped with six independently controlled heating zones. The PLA/PEG 70/30 blends, previously dried, were gradually introduced into the hopper to maintain consistent feeding. The temperature profile was set to 195°C, 185°C, 180°C, 180°C, 175°C, and 170°C from the hopper to the die, with the screw operating at 20 rpm.

The extruded strands were cut into 50 cm segments and cooled on an aluminum sheet to prevent them from sticking together. Once fully cooled, the strands were fed into a ThermoFisher Varicut 11 mm pelletiser to produce uniform PLA/PEG pellets with consistent composition, suitable for the subsequent 3D-printing filament production step.

1.2.3.2 Second extrusion

The production of 3D-printable filament was carried out during the second extrusion step using a 3Devo Composer Filament Maker, which is equipped with an integrated diameter control system. This system combines a laser sensor with pulling gears and operates through a feedback loop, allowing for precise regulation of the filament diameter within a tolerance of $\pm 50 \mu\text{m}$. The extruder features four independently controlled heating zones: zone 1, located near the hopper, and zone 4, corresponding to the die temperature. The temperature profile was set to 175°C, 182°C, 187°C and 80°C from zone 1 to zone 4, respectively. Extrusion was carried out at a screw speed of 3.5 rpm, with the cooling fan operating at 52% capacity. The extruded filament was directly wound onto a spool with the spool speed parameter set to

1600. Due to the presence of PEG, the PLA/PEG blend tends to exhibit a certain degree of stickiness, particularly when the filament has not yet cooled adequately. Therefore, these parameters were selected to ensure that the filament remained sufficiently warm for uninterrupted extrusion without causing die blockage, while also being cool enough to prevent sticking to the pulling gears.

1.2.4 Production of PLA/PEG dogbones for tensile tests

Two types of dogbone specimens were prepared for mechanical testing: one set produced by injection molding and another by 3D printing.

The injection-molded dogbones were fabricated using both a commercial PLA filament and the PLA HP2500 grade used in the PLA/PEG blends. The commercial PLA filament was first pelletized using a ThermoFisher Varicut 11 mm pelletizer. Both the resulting pellets and the PLA HP2500 pellets (used as received) were dried under vacuum at 50°C for 24h prior to injection. The specimens, conforming to the ISO 527-2-5A standard, were produced using a Thermo Scientific HAAKE MiniJet Pro micro-injection molder. The processing parameters were as follows: a cylinder temperature of 190°C, a mold temperature of 50°C, an injection pressure of 600 bar and a holding pressure of 500 bar, all maintained for 30 seconds.

Before 3D printing, the dogbone specimens were modeled using Fusion 360, following the ISO 527-2-5A specifications. For macroporous samples, a design modification was introduced in the gauge section: a 1 cm segment was replaced at the center by using the Volumetric Lattice tool with gyroid lattices, a solidity of 50% and a unit cell size set to 16 mm and 20 mm for samples "P16" and "P20", respectively. All dogbone samples were sliced with the software FlashPrint 5 and printed using a FlashForge Creator 3 printer. Printing parameters were as follows: nozzle temperature of 200°C, build plate temperature of 30°C, 100% infill density and three outer shells. All other printing settings remained at their default values.

The samples used for tensile testing are presented in Table 1.1, along with their nomenclature and a brief description of their respective purposes.

Table 1.1 Description of the studied samples used for traction tests.

Sample Name	Description
IM HP2500	PLA HP2500 processed by injection molding → Used as defect-free reference
IM cPLA	Commercial PLA processed by injection molding → Used as comparison with PLA HP2500
cPLA	Commercial PLA printed in 3D → To highlight the effect of 3D printing compared to IM samples
cPLA P16	Commercial PLA printed in 3D with a macroporosity of 16 → To highlight the effect of macroporosity P16
cPLA P20	Commercial PLA printed in 3D with a macroporosity of 20 → To highlight the effect of macroporosity P20
Blend	PLA/PEG100K 70/30 blend (all the following blends have the same composition) → Used as reference for all other 3D printed blends
Blend ext.	PLA/PEG blend after PEG extraction → To highlight the effect of PEG extraction in the blend
Blend ann.	PLA/PEG blend annealed at 110°C for 4h after printing → To highlight the effect of annealing on 3D printed blends
Blend ann. ext.	PLA/PEG blend annealed at 110°C for 4h after printing and PEG extraction → To highlight the combined effect of annealing and PEG extraction
Blend P20	PLA/PEG blend with a macroporosity of 20 → To highlight the effect of macroporosity P20 on 3D printed blends
Blend P20 ext.	PLA/PEG blend with a macroporosity of 20 after PEG extraction → To highlight the combined effect of macroporosity and PEG extraction
Blend P16	PLA/PEG blend with a macroporosity of 16 → To highlight the effect of macroporosity P16 on 3D printed blends
Blend P16 ext.	PLA/PEG blend with a macroporosity of 16 after PEG extraction → To highlight the combined effect of macroporosity and PEG extraction

1.2.5 Extraction of PEG

For PEG film extraction, the isothermally crystallized PLA/PEG blends were immersed into distilled water at room temperature for 1h. This process was repeated twice, then the samples were immersed one last time into distilled water for 24h. The water was replaced between each step to eliminate the dissolved PEG.

For 3D-printed samples, the PLA/PEG objects were immersed in 500 mL of distilled water at room temperature and stirred continuously for 24 hours. In this case, the volume and agitation of the water were sufficient to promote effective PEG diffusion and prevent its accumulation within the pores, eliminating the need for water replacement.

1.3 Characterization techniques

1.3.1 Thermal behavior at high cooling rates

fDSC analysis was used to measure the glass transitions of the blends ($T_{g,blend}$) and to investigate the isothermal crystallization of the blends at different temperatures. fDSC experiments were carried out with a flash-DSC1 from Mettler Toledo connected to an intracooler and N₂ purge gas. Before analysis, PLA/PEG films were dried overnight at 40°C under vacuum. Then, a small piece of the films (ca. a few hundreds of ng) was cut with a razor blade and manipulated with a paintbrush hair under microscope. The fDSC samples were too small for their mass to be measured. The samples were then placed at the center of the fDSC chip. The temperature ramps used in fDSC are described in Figure 1.1.

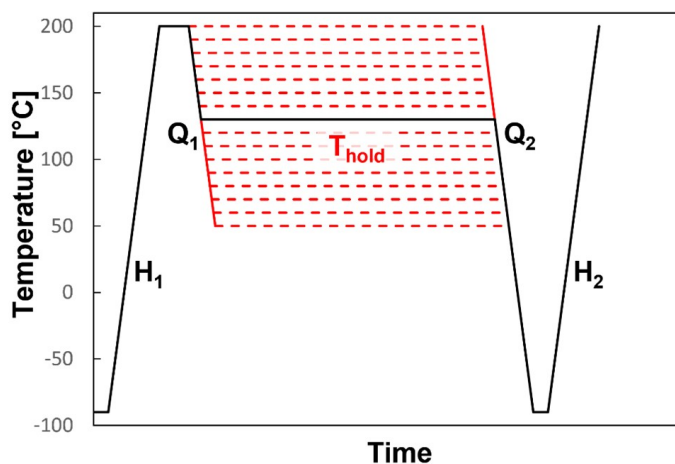


Fig. 1.1 fDSC temperature ramps used to determine the phase diagram of PLA/PEG blends.

Initially, the thermal history of all samples was erased by a first heating (H_1) at 1000°C/s. Subsequently, samples were held at 200°C, above the melting temperature of PLA ($T_{m,PLA}$), for 1s to eliminate any residual crystals. The samples were then quenched for the first time (Q_1) at 1000°C/s from the

Table 1.2 fDSC parameters for PLA/PEG blends, pure PLA and pure PEG.

Samples	T_{min}	H_{1-2}	T_{max}	Q_{1-2}	T_{hold}	Duration
PLA/PEG blends	-90°C	1000°C/s	200°C	-1000°C/s	50 - 200°C	300s
Pure PLA	25°C	1000°C/s	200°C	-1000°C/s	50 - 130°C	600s
Pure PEG	-90°C	1000°C/s	125°C	-1000°C/s	-20 - 40°C	10s

molten state to a temperature T_{hold} at which the blend state is investigated. Samples were maintained at this temperature for 5 minutes to allow them to reach thermodynamic equilibrium. T_{hold} was varied from 200 to 50°C for each sample to observe the evolution of the blend state in this temperature range. Once at equilibrium, the samples were submitted to a second quench (Q_2) at 1000°C/s from T_{hold} to -90°C, effectively "freezing" their equilibrated states. This state was ultimately observed on the second heating (H_2) at 1000°C/s. The glass transition temperatures (T_g) as well as the melting peaks (T_m) were defined as the midpoint of the specific heat jumps and the maximum of the endothermic peaks in the fDSC curves, respectively.

The same method was applied for pure PLA and pure PEG fDSC analyses, with adapted temperature ranges and holding times. For PLA, the minimum temperature was set to 25°C, with isothermal steps ranging from 130°C to 50°C and T_{hold} of 10 minutes. For the analysis of PEG crystallization during cooling, the maximum temperature was 125°C, with isotherms from 40°C down to -20°C and a holding time of 10 seconds. All parameters are summarized in Table 1.2.

To determine the critical cooling rate for PEG, the sample was first heated from -90°C to 100°C at a rate of 1000°C/s, then cooled at various rates. This heating-cooling cycle was repeated for each cooling rate tested: -4000°C/s, -2000°C/s, -1000°C/s, -500°C/s, -200°C/s, -100°C/s, and -1°C/s. It is worth noting that even the slowest rate employed here remains six times faster than in conventional DSC.

Table 1.3 DSC parameters for PLA/PEG blends, pure PLA and pure PEG.

Samples	T_{min}	H_{1-2}	T_{max}	Q_{1-2}	T_{hold}	Duration
PLA/PEG blends	-20°C	10°C/min	200°C	-10°C/min	50 - 130°C	20 min
Pure PLA	-20°C	10°C/min	200°C	-10°C/min	50 - 130°C	20 min
Pure PEG	-90°C	10°C/min	125°C	-10°C/min	-	-

1.3.2 Conventional thermal behavior

A differential scanning calorimeter DSC1 from Mettler Toledo was used to determine the glass transition temperature, the melting temperature and the optimal crystallization temperature of the samples.

The PLA/PEG blend samples (90/10, 70/30 and 50/50) used for conventional DSC measurements were prepared from solvent-cast films, which were cut into circular discs and placed into aluminum crucibles. For PLA, a fragment of the original pellet was directly inserted into the crucible. PEG samples (3K, 100K and 1M) were used in powder form and also placed directly into the crucibles. Each sample was weighed and sealed in its crucible. A small hole was pierced in the lid to prevent pressure build-up and potential rupture during heating.

DSC measurements were carried out under a nitrogen atmosphere (flow rate of 50 mL/min) using the same thermal protocol as described for fDSC (shown in Figure 1.1), with the main difference being the significantly slower heating (H_1 , H_2 = 10°C/min) and cooling (Q_1 , Q_2 = -10°C/min) rates. These slower rates do not prevent microstructural rearrangements during cooling, in contrast to the rapid conditions achieved in fDSC.

For neat PLA, the temperature range was set from -20°C to 200°C, with isothermal steps between 50°C and 130°C, each held for 20 minutes. PEG samples were heated from -90°C to 200°C and then directly cooled to -90°C without isothermal holds, as PEG crystallizes too rapidly during cooling. For PLA/PEG blends, the temperature program was the same as for neat PLA, including isothermal steps from 50°C to 130°C. All thermal parameters are summarized in Table 1.3.

1.3.3 Crystallization kinetics and morphology

The morphology of the material and the spherulitic growth rate were evaluated by polarized optical microscopy (POM). The samples were observed between crossed polarizers using an Olympus AX70/Provis microscope equipped with an objective x10 and a charge-coupled device (CCD) camera. To monitor spherulitic growth in real time, a Mettler Toledo FP90 heating stage was coupled to the microscope, allowing in situ crystallization observation. PLA/PEG films previously prepared by solvent casting were first melted at 200°C between two glass slides on an external hot plate, then rapidly transferred to the target crystallization temperature (90°C, 110°C and 130°C) onto the heating stage under the microscope. Given the strong temperature dependence of crystallization kinetics, thin cover slips were used instead of standard glass slides to minimize thermal inertia. Once inserted at the desired temperature, images were recorded with the CDD camera at regular time intervals to calculate the radial growth rate. Image acquisition continued until all spherulitic domains were in contact, except in the case of neat PLA, whose crystallization was too slow to observe complete coverage within a practical timeframe; in this case, the experiment was stopped after 70 minutes.

1.3.4 Surface features and microscale porosity

Scanning Electron Microscopy (SEM) was used to investigate the microstructure and internal porosity of PLA/PEG blends, with a particular focus on identifying morphological features such as spherulitic domains and voids formed upon PEG extraction. Both surface and cross-sectional observations were performed to gain insight into the spatial distribution and connectivity of the porous network.

SEM imaging was performed using a JEOL 7600F microscope operated at 5 kV with a working distance of 8 mm. Crystallized PLA/PEG films were produced as described in the section 1.2.2. To access internal morphology, first immersed in liquid nitrogen and then fractured to produce clean cross-sections. In contrast, the larger 3D-printed samples were directly cut with a razor blade.

Prior to SEM observation, all samples were deposited on a conductive tape and coated with a 12 nm gold layer using a Ted Pella Cressington 208HR high-vacuum sputter coater. This conductive coating prevented charge accumulation and surface damage during imaging. For 3D-printed

specimens, the sample stage was manually rotated during coating to ensure uniform coverage over the entire surface.

1.3.5 Crystalline Structures in PLA/PEG blends

X-ray diffraction (XRD) was employed to characterize the crystalline phases present in neat PLA, PEG, and their blends, with the dual objective of identifying the specific crystal structures formed during isothermal crystallization and estimating the proportion of crystallinity associated with each polymer phase.

Samples of pure PLA and PLA/PEG100K blends were melted and isothermally-crystallized directly on the sample holder at 110°C before cooling to room temperature. Pure PEG powders were heated to 90°C then manually pressed to form a disc of 1 mm thickness and exhibited sufficient mechanical integrity for direct placement onto the XRD sample holder. X-ray scattering was measured in a home-made setup, with incident X-rays generated by a Rigaku rotating Copper anode fitted with a collimating and monochromatizing mirror with a vertical divergence of 0.007°, generating K_{α} photons. The sample was aligned at the center of a $\theta/2\theta$ Siemens two-circles diffractometer. The beam was vertically shaped by a slit of 500 μm height, with the size of the beam at the sample position being ca. 520 μm . Owing to the collimation of the primary beam, the detecting side of the goniometer was only fitted with a proportional counter preceded by a horizontal Soller slit of 0.33° vertical resolution. Vertical Soller slits of 0.33° horizontal resolution were placed in the incoming and outgoing beam paths.

The data were corrected for polarization and volume variations depending on angle; they are plotted versus $s = 2 \sin(\theta) / \lambda$ in which θ is half the scattering angle and $\lambda = 0.15418 \text{ nm}$ is the wavelength of the Cu K_{α} line. The data were scaled to absolute units by using the procedure of Ruland modified by Vonk [121, 122]; this is only approximate since the diffraction angles were limited to the range $2\theta = 10\text{--}40^\circ$ only. Since the Compton scattering is proportionally very small in this diffraction range, it was ignored.

The corrected and scaled scattering of the pure PLA and PEG samples was decomposed into a amorphous halo and a sum of crystalline Pearson VII peaks. The scattering of the blends was then decomposed using a linear combination of the PEG and PLA amorphous halos plus a sum of crystalline

Pearson VII peaks for which the shape, position and width were kept constant to the values found for the pure polymers. From the decomposition, the intensity $I_c(s)$ of the crystalline peaks belonging to either PEG or PLA was obtained.

The mass fraction of crystalline PEG and crystalline PLA in the samples was computed by :

$$X_c = \frac{\int 2\pi s^2 I_c(s) ds}{\int 2\pi s^2 I(s) ds} \quad (1.1)$$

with $I(s)$ the total intensity scattered by the sample. These mass fractions are close to the mass crystallinity; however, due to the limited scattering range measured, they are not strictly equal to the mass crystallinity.

1.3.6 Quantitative analysis of PEG extraction

The remaining PEG content in PLA after PEG extraction was evaluated by ^1H nuclear magnetic resonance (NMR). ^1H NMR spectra were recorded in CDCl_3 at a polymer concentration of 40 mg/mL. All NMR measurements were performed on a Bruker Avance II spectrometer operating at 7.0 T, corresponding to a ^1H Larmor frequency of 300 MHz. Spectra were acquired using TopSpin software (Bruker) and a BBFO(^1H ,X) probehead equipped with a z-gradient coil.

Neat PLA and PEG were directly dissolved in CDCl_3 , while PLA/PEG blends were first processed into films by solvent casting, then redissolved in CDCl_3 for analysis. Characteristic proton signals were identified at 5.16 ppm ($-\text{CH}$) and 1.58 ppm ($-\text{CH}_3$) for PLA, and at 3.64 ppm ($-\text{CH}_2$) for PEG. The PEG content in the blends was quantified by integrating the corresponding NMR peaks. Based on these peaks, the PEG mass fraction in each sample was determined using the following equations:

$$n_{\text{PEG}} = \frac{I_{\text{PEG}}/4}{I_{\text{PLA},\alpha} + I_{\text{PEG}}/4}$$

with n_{PEG} the molar fraction of PEG repeat units in the blend, I_{PEG} the integrated area of the peak at 3.64 ppm, $I_{\text{PLA},\alpha}$ the area under the peak at 1.58 ppm corresponding to the H_α of PLA. The value of $I_{\text{PLA},\alpha}$ was arbitrarily chosen over $I_{\text{PLA},-\text{CH}_3}$, but this choice had a negligible impact on the final

calculations (variations remained below 0.5%). Then,

$$w_{PEG} = \frac{n_{PEG} MM_{PEG}}{n_{PEG} MM_{PEG} + (1 - n_{PEG}) MM_{PLA}}$$

with w_{PEG} the PEG mass fraction, MM_{PEG} the molar mass of a PEG repeat unit (44 g/mol) and MM_{PLA} the molar mass of a PLA repeat (72 g/mol).

1.3.7 3D porosity mapping

A 3D reconstruction of the extracted PLA/PEG100K 70/30 film was performed using a Phoenix Nanotom M micro-CT system (Baker Hughes). This experiment was conducted externally in collaboration in the lab of Greet Kerckhofs at UCLouvain (Woluwe site). This non-destructive technique enabled detailed imaging of the complex porous architecture within the material. Scanning was carried out at 50 kV and 245 μ A, with an exposure time of 750 ms. Frame averaging was set to 3, and an image skip of 1 was applied. The resulting voxel size was 0.75 μ m³, close to the resolution limit, allowing for high-resolution visualization of the microstructure.

Porosity quantification was carried out by manual grayscale thresholding on the reconstructed micro-CT datasets. The intensity threshold was selected to differentiate between pore space and solid material, based on visual contrast within the image volume. Voxels with grayscale values below this threshold were classified as pores, while higher-intensity voxels were attributed to the polymer matrix. In this case, the contrast between the two phases was sufficiently high to allow reliable segmentation by manual thresholding. The total porosity was then calculated as the ratio of pore voxels to the total number of voxels within the selected volume of interest.

For improved clarity in the visualizations, pore regions were colored in green and the solid phase in grey. To assess internal porosity and visualize pore interconnectivity, a parallelepiped volume of 200 $\times$ 80 $\times$ 80 μ m³ was selected from the center of the sample. The upper solid portion of this region was digitally removed to expose the internal porous network and facilitate the evaluation of its connectivity.

1.3.8 Other geometries and 3D-printing conditions

Before producing the dogbone specimens, preliminary 3D-printed samples were fabricated to evaluate the feasibility of generating hierarchical porosity within PLA/PEG blends. These included both solid and macroporous cubes, which were first designed using Fusion 360 and sliced with FlashPrint 5. All samples were produced with the PLA/PEG100K 70/30 blend and printed on a FlashForge Creator 3 printer using the same set of parameters employed for the dogbones specimens: nozzle temperature of 200°C, build plate temperature of 30°C, 100% infill density, and three outer shells; other settings were left at their default values. Solid cubes of 1 cm³ were used to assess the formation and distribution of internal microporosity following PEG extraction. To evaluate the implementation of a second porosity level, macroporous cubes were designed by Fusion 360 using the Volumetric Lattice tool with gyroid lattices, a solidity of 50% and unit cell sizes of 16 mm (P16) and 20 mm (P20). These same architectures were subsequently reused in the central gauge region of the dogbone specimens, thereby enabling mechanical testing of dual-porosity structures.

1.3.9 Tensile tests

Tensile tests were performed to characterize the mechanical behavior of the materials under uniaxial loading conditions. The tested specimens included injected-molded, 3D-printed and porous geometries as explained in the section 1.2.4 regarding the production of PLA/PEG dogbones for tensile tests. For each formulation and processing conditions, three samples were tested at room temperature.

For 3D-printed and injection-molded specimens, the standardized tensile geometry was fabricated according to ISO 527-2-5A. These tests were performed on an Instron 6800 series machine at an elongation rate of 25 mm/min.

From the stress–strain curves, the following mechanical properties were extracted: Young’s modulus (E), elongation at break (ϵ_b), maximum tensile stress (σ_m), and toughness (T). Additionally, the post-fracture samples were analyzed by DSC to assess the crystallinity of the sample.

1.3.10 Overall methodology

The experimental methods described in this section were specifically selected and adapted to address the central objectives of this thesis. From the precise thermal control offered by fDSC to the spatial resolution of SEM and μ CT, each technique contributed to a deeper understanding of the interactions between PLA and PEG. Combined with controlled sample preparation and additive manufacturing, this methodology made it possible to correlate composition, processing parameters and multi-scale morphology to ultimately enabling the design of complex porous materials.

1.4 Writing method

This thesis was written with the assistance of ChatGPT, following a structured and iterative process. Initially, the content was drafted in French in an informal tone, similar to how it might be expressed orally. These drafts were then submitted to ChatGPT, where the instructions included translating the text into English, grouping ideas into coherent thematic sections, and reformulating the content to adopt a more academic tone. The resulting text was subsequently reviewed and edited by the author as needed.

At the end of each chapter, ChatGPT was also asked to evaluate the overall structure and clarity of the section and to propose potential improvements. Some of these suggestions were implemented, while others were deliberately left aside based on the author's critical assessment and judgment.

PART IV

Results

1

Crystallization of PLA, PEG and PLA/PEG blends

Crystallization is a fundamental process in polymer science, as it directly influences the microstructure and, consequently, the physical properties of semi-crystalline polymers. For materials such as poly(L-lactic acid) (PLA¹) and polyethylene glycol (PEG), the crystallization behavior dictates the organization of crystalline and amorphous regions, impacting their microstructure, thermal stability and mechanical performance. In polymer blends, the crystallization of individual components can lead to phase separation, which affects the overall morphology of the material [123]. For example, in PLA/PEG blends, the interplay between crystallization and miscibility governs the distribution of each component within the matrix, influencing their spatial arrangement, creating distinct PLA-rich and PEG-rich phases [74]. Understanding these crystallization processes is essential for interpreting the phase behavior and microstructural evolution of such systems, but more importantly, by appropriately selecting processing conditions, it enables the creation of controlled porosity following PEG extraction [5].

In this chapter, the crystallization phenomena of PLA, PEG, and their blends will be explored in details. The crystallization process will be charac-

¹In this text, the notation PLA was chosen over PLLA for simplicity as the same PLA was used for all the experiments.

terized using differential scanning calorimetry (DSC) and flash-DSC (fDSC), while polarized optical microscopy (POM) will be used to examine the morphology of the spherulites, including their size and distribution, as well as the radial spherulitic growth rate. Additionally, X-ray diffraction (XRD) will be used to determine the specific crystalline phases present. The influence of PEG, including its molar mass and concentration in the blend, will also be studied to understand its effects on the overall crystallization behavior.

1.1 Crystallization of neat PLA

1.1.1 Thermal characteristics of PLA

Before diving into the complex world of polymer blends, it is important to understand the crystallization behavior of PLA alone, as these results will serve as a reference for comparing how the crystallization evolves when blended with PEG. Performing isothermal crystallization, rather than crystallizing during cooling, allows a precise control over the crystallization conditions, thereby enabling a clearer analysis of the kinetics and mechanism of crystal formation. Therefore, PLA was initially melted at 200°C to remove any thermal history. It was then cooled at 10°C/min to specific isothermal hold temperatures (T_{hold}) between 130°C and 70°C before being cooled to room temperature. Finally, PLA was heated up to 200°C to record the melting of the crystals formed during the isotherms. This method is explained in details in the Methods section. The T_{hold} temperatures were selected to investigate conditions above, below, and within the optimal crystallization window of PLA, to see both rapid and inhibited crystallization behaviors. The phase transitions during isotherms and subsequent heatings were monitored by DSC and are presented in Figure 1.1 in right and left panels respectively.

The heating curves, shown on the right-hand side of Figure 1.1, reveal several thermal events for PLA at different T_{hold} . Firstly, an endothermic melting peak is observed consistently around 175°C for all T_{hold} values, indicating the melting of PLA crystals. The specific values of the melting temperature (T_m) and other characteristic temperatures are summarized in Table 1.1.

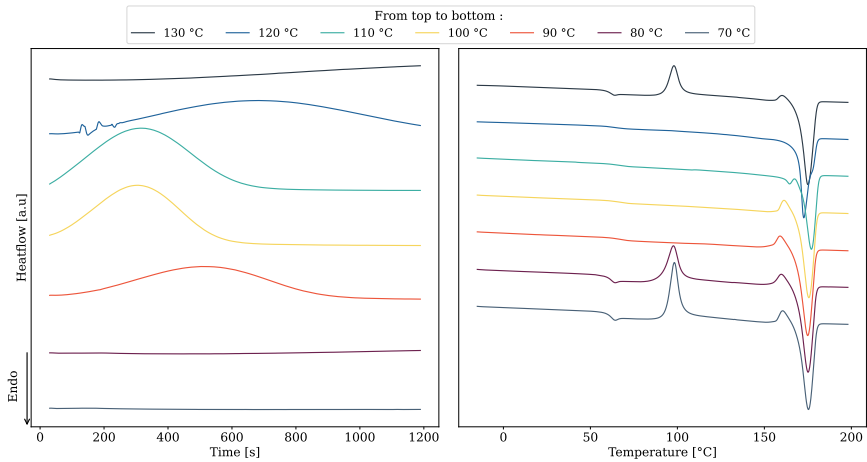


Fig. 1.1 DSC isothermal curves during the crystallization (left) and the subsequent second heating curves of PLA after isothermal crystallization at the indicated temperature for 20 min (right). The curves are displaced vertically for clarity.

Table 1.1 Characteristic temperatures of pure PLA extracted from DSC curves.

T_{hold}	130°C	120°C	110°C	100°C	90°C	80°C	70°C
T_m [°C]	175	173	177	175	175	175	175
T_g [°C]	62	65	66	68	67	62	63
T_{cc} [°C]	98	-	-	-	-	98	98
$t_{c,max}$ [s]	-	682	315	306	506	-	-

Next, cold crystallization peaks are visible in the heating curves at the highest and lowest T_{hold} values, specifically above 130°C and below 80°C. These exothermic peaks appear around 100°C, suggesting that PLA did not crystallize entirely during the isotherms but instead crystallizes during the heating phase. This indicates suboptimal crystallization conditions.

Furthermore, the glass transition temperature (T_g) is visible in the heating curves around 60°C. This transition is more noticeable for T_{hold} values of 130°C, 80°C, and 70°C.

Finally, a minor exothermic peak appears just before the main melting peak, suggesting a process of crystal reorganization during heating.

The occurrence of cold crystallization peaks at the highest ($> 130^{\circ}\text{C}$) and lowest ($< 80^{\circ}\text{C}$) T_{hold} values suggests that these temperatures are not ideal for promoting full crystallization during the hold period. Consequently, the crystals form during the heating and not during the isotherms. At high T_{hold} values, the probability of nucleation is low and the crystallization is slow. Conversely, at low T_{hold} values near T_g , molecular mobility is too restricted to facilitate crystallization, leading to incomplete crystal formation during the isotherms and subsequent cold crystallization during heating.

The presence of T_g at approximately 60°C , particularly noticeable for T_{hold} values of 130°C , 80°C , and 70°C , suggesting a limited degree of crystallization during the isotherm at these temperatures. Indeed, the visibility of T_g decreases as crystallinity increases, indicating a higher degree of amorphous content for these particular T_{hold} values. This observation aligns with the earlier presence of cold crystallization peaks for these same temperatures, which already suggests that the PLA remained predominantly amorphous during the isotherms. Interestingly, the T_g values (see Table 1.1) observed for PLA that underwent crystallization during the isotherms are slightly higher than those seen for fully amorphous PLA. This elevation in T_g is attributed to the densification of the amorphous phase that occurs as crystalline regions grow. During crystallization, the development of PLA crystals confines the surrounding amorphous regions, restricting the mobility of polymer chains and effectively increasing the glass transition temperature. This densification of the amorphous phase results in lower free volume and higher energy requirements for chain movement, which manifests as an increased T_g in the DSC curves [124].

The minor exothermic peak observed just before the melting peak is indicative of crystal reorganization, also known as crystal perfection or recrystallization, typical of PLA. This process occurs because the initial crystals formed during cooling are less stable and are known as α' crystals. As the temperature rises during heating, these crystals rearrange to adopt a more thermodynamically stable structure, the α crystals, releasing energy in the process [54, 55].

To complement the results obtained from the heating curves, it is useful to examine what occurs during the isotherms, as this provides important information about the crystallization kinetics of PLA. On the right-hand graph of Figure 1.1, the exothermic crystallization peaks of PLA occurring during the isotherms can be clearly observed. From these curves, the overall

crystallization rate can be quantified. Typically, the value $t_{c1/2}$, known as the half time of crystallization, is used as a measure of the time required for half of the crystallization to occur, which corresponds to half of the total enthalpy of crystallization. However, given that the crystallization peaks are sometimes incomplete, the time at the peak maximum ($t_{c,max}$) is taken here instead of $t_{c1/2}$. These values are summarized in Table 1.1.

For intermediate temperatures, ranging from 90°C to 120°C, full exothermic peaks are observed, indicating that the PLA completely crystallizes within the 20 minutes isotherms. Specifically, at 100°C and 110°C, the crystallization rate is the highest, with the process complete within just 10 minutes. Conversely, at temperatures of 80°C and 130°C, only the initial stage of crystallization is visible, as evidenced by the onset and shape of the exothermic peaks. At 70°C, PLA does not crystallize at all during the isotherm.

The presence of complete exothermic peaks at intermediate temperatures (90°C to 120°C) suggests that these conditions are optimal for PLA crystallization, with the fastest rates at 100°C and 110°C. The reduced crystallization observed at 80°C and 130°C implies that these temperatures are less favorable for crystallization due to suboptimal chain mobility (lower temperatures) or slow nucleation (higher temperatures). The inability of PLA to crystallize at 70°C during the isotherm, also indicated by the more pronounced cold crystallization peak during heating, reflects the close proximity of this temperature to T_g , where the chain mobility is insufficient to support crystallization.

To minimize potential reorganization prior to isothermal crystallization, flash differential scanning calorimetry (fDSC) was employed due to its capability of extremely rapid cooling and low sample mass, which effectively reduces thermal inertia. Direct quenching from the melt to the targeted T_{hold} allows PLA crystallization to initiate immediately at the start of the isotherm, avoiding pre-crystallization reorganization that could occur with slower cooling rates in conventional DSC.

Unlike conventional DSC, which typically uses sample sizes of about 10 mg, fDSC operates with significantly smaller samples, approximately 100 ng. This smaller scale decreases thermal inertia; additionally, one array of sensors is placed on the chip, which enhances sensitivity, allowing the detection of small crystalline fractions. Moreover, the rapid temperature change capabilities of fDSC make it possible to freeze the sample at a given moment, effectively capturing its state before quenching, like a 'snapshot'.

Table 1.2 Characteristic temperatures of pure PLA extracted from fDSC curves.

T_{hold}	130°C	120°C	110°C	100°C	90°C	80°C	70°C
T_m [°C]	180	174	167	157	152	148	148
T_g [°C]	68	72	72	74	74	73	70

However, a limitation of fDSC is the difficulty to accurately measure the mass of such small samples, making it unsuitable for absolute quantification of crystallinity. Instead, fDSC is particularly valuable for qualitative comparisons under different conditions.

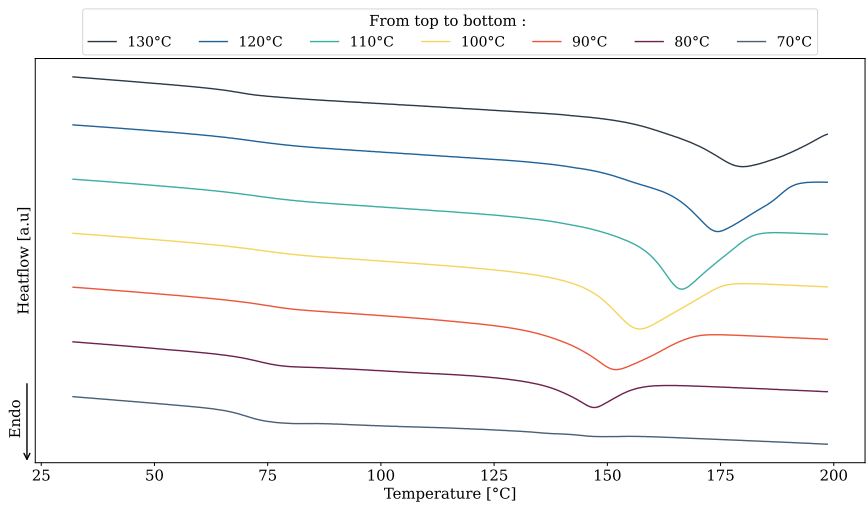


Fig. 1.2 fDSC heating curves of PLA after isothermal crystallization at the indicated temperatures for 10 minutes. The curves are displaced vertically for clarity.

To investigate the crystallization of PLA using fDSC, the same experimental method was employed as with conventional DSC, but with some adjustments. The cooling and heating rates were increased from 10°C/min to 1000°C/s, and due to the reduced sample size, the duration of the isotherms was lowered from 20 minutes to 10 minutes. The resulting heating curves of PLA crystallized isothermally at various T_{hold} values are shown in Figure

1.2. In these curves, endothermic melting peaks are visible for T_{hold} between 130°C and 80°C, while no crystallization is observed at 70°C. Additionally, the melting temperatures exhibit a dependency on the crystallization temperature, decreasing from 180°C to 148°C as T_{hold} decreases. Lastly, T_g of PLA is observed around 75°C for most conditions. Specific values of T_m and T_g are summarized in Table 1.2.

The melting temperatures observed in the heating curves indicate that T_m decreases as T_{hold} decreases, which is consistent with what is typically expected for samples crystallized at different temperatures. This dependency arises because the lamellar thickness of the crystals, and thus their thermal stability, is directly influenced by the crystallization temperature. At higher T_{hold} values, larger and more thermodynamically stable crystals are formed, which melt at higher temperatures. Conversely, at lower T_{hold} values, smaller and less stable crystals are produced, which melt at lower temperatures [52, 125].

A notable distinction between fDSC and conventional DSC is observed in the crystallization behavior of PLA. Under conventional DSC, T_m does not vary significantly with T_{hold} , unlike in fDSC where a clear dependency on T_{hold} is observed. This indicates that in conventional DSC, reorganization processes are possible during the slower temperature changes, whereas in fDSC, crystallization initiates during the isotherms without subsequent reorganization. Furthermore, the absence of reorganization peaks just before the main melting peak in fDSC further confirms the lack of crystal reorganization. Additionally, under conventional DSC, PLA barely crystallizes at T_{hold} values of 80°C and 130°C due to slower kinetics, while in fDSC, PLA effectively crystallizes at these temperatures. This discrepancy is attributed to the smaller sample size, the proportionally longer crystallization time relative to sample size, and the enhanced sensitivity of fDSC. Specifically, in conventional DSC, even when crystallization begins at 80°C or 130°C, the crystalline fraction remains too small to produce a detectable signal. In contrast, the reduced sample size in fDSC means that the relative proportion of crystalline to amorphous regions is larger, allowing these crystalline events to be more easily observed.

Finally, T_g values obtained with fDSC are consistently higher than those recorded with conventional DSC. This difference is due to the suppression of amorphous phase relaxation during the rapid cooling rates employed by fDSC, resulting in a more constrained amorphous network forming at a

higher temperature when cooling and subsequently, an elevated T_g upon heating.

These results highlight the capability of fDSC to effectively capture subtle differences in the crystallization behavior of PLA that are not easily detectable with conventional DSC. The rapid thermal transitions available with fDSC provide a more accurate representation of crystallization behavior, particularly for conditions where conventional DSC is unable to prevent reorganization during cooling or heating steps. Furthermore, fDSC allows for snapshots of the sample state at specific temperatures, which will be particularly useful for constructing the phase diagram of PLA/PEG blends.

1.1.2 Crystalline morphology of PLA

In the previous section, the crystallization behavior of PLA, including its half time of crystallization, was characterized through DSC analysis. To complement this, the morphological analysis under isothermal conditions showcases the mechanisms governing crystallization kinetics and the progressive development of spherulitic structures. To visualize spherulite growth and investigate the impact of temperature on nucleation density and growth rate, polarized optical microscopy (POM) was employed. Under polarized light, crystalline regions appear bright due to birefringence, except when the electric field is aligned with an optical axis of the crystal, while isotropic amorphous regions remain dark, allowing clear visualization of crystallization progression and spherulite morphology.

For the study of PLA crystallization, samples were first melted at 200°C between two glass slides. Subsequently, they were quenched to the targeted crystallization temperatures of 90°C, 110°C, and 130°C. These specific temperatures were selected based on previous DSC results. 110°C represents the optimal crystallization temperature, while 90°C and 130°C correspond to either challenging crystallization due to suboptimal mobility or a decreased nucleation rate. At 90°C, the low temperature restricts molecular mobility, while at 130°C, the high temperature results in low nucleation probability, also hindering effective crystallization. This allows for the exploration of morphological changes at low, optimal and high crystallization temperatures.

Figure 1.3 illustrates the time-dependent evolution of spherulites during isothermal crystallization at different temperatures.

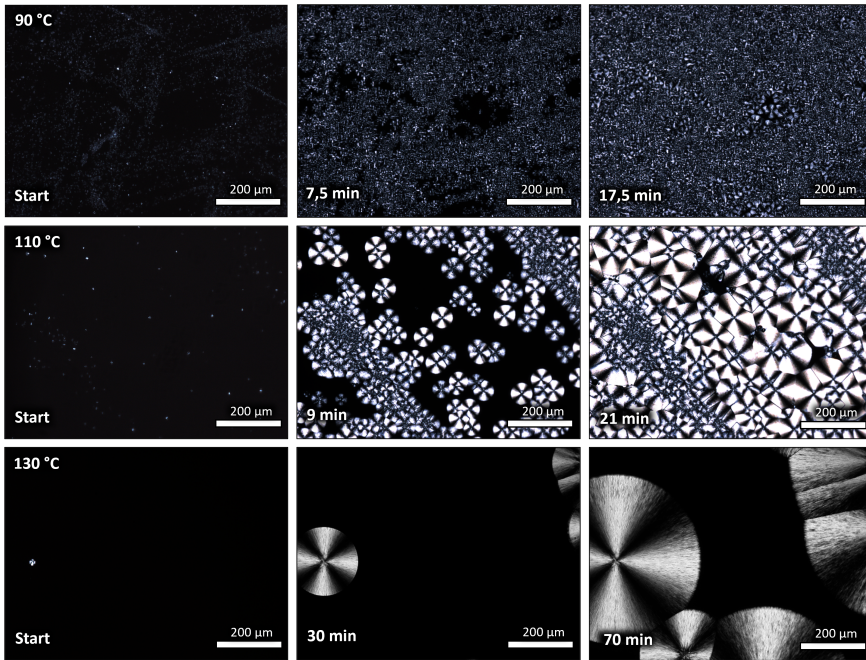


Fig. 1.3 POM images of PLA isothermal crystallization at 90°C (top row), 110°C (mid row), and 130°C (bottom row).

At 90°C (Figure 1.3, top row), crystallization occurs rapidly, with the sample having fully contacting spherulites after 17.5 minutes. The high nucleation density leads to the formation of numerous small spherulites. Despite the reduced chain mobility close to T_g , it is still sufficient for crystallization to proceed efficiently. The large amount of nucleation sites leads to fast overall crystallization.

At 110°C (Figure 1.3, middle row), a lower nucleation density compared to 90°C results in the formation of larger spherulites, with fully contacting spherulites after 21 minutes. Maltese crosses appear, which are indicative of radially-ordered crystalline lamellae in semi-crystalline polymers, reflecting the alignment of optical axes and polarizer orientations.

At 130°C (Figure 1.3, bottom row), the nucleation density is significantly lower, leading to the formation of only a few large spherulites. Even after 70 minutes, all the spherulites are not in contact with each other. The low

amount of nucleation sites leads to slow overall crystallinity.

As expected, the number of nucleation sites is temperature-dependent. As the temperature decreases, the driving force for nucleation increases, resulting in more nucleation sites [46, 126]. This observation aligns well with the results obtained at the different temperatures of 90°C, 110°C, and 130°C.

When comparing these results obtained using POM to the half-crystallization times ($t_{c1/2}$) measured by DSC, the duration of "full" crystallization, when the spherulites are in contact, falls within the same range. For example, at 90°C and 110°C, crystallization occurs within a few minutes, whereas at 130°C, the crystallization process takes significantly longer. So much that it could not be measured using DSC due to the time constraints. It is also noteworthy that the crystallization at 90°C is faster in POM than in DSC, which could be attributed to the preferential alignment of polymer chains when the sample is confined between two glass slides.

During crystallization, every spherulite grow continuously until neighboring spherulites come into contact, leading to impingement. Thus, the overall crystallization rate can be considered as the product of the number of spherulites (and consequently, the number of nucleation sites) and the spherulitic radial growth rate.

It would be interesting to also calculate this spherulitic radial growth rate to gain further insight into the crystallization kinetics under different conditions independently of nucleation sites. The growth rate of PLA spherulites at each temperature was quantified by measuring the spherulite radius as a function of time, as shown in Figure 1.4. The growth rate was determined from the slope of the linear region in these plots, resulting in values of 1.29 $\mu\text{m}/\text{min}$, 3.60 $\mu\text{m}/\text{min}$, and 4.22 $\mu\text{m}/\text{min}$ at 90°C, 110°C, and 130°C, respectively. Those values are slightly higher than the values reported by Zhang et al. [127] but falls in the same range as the ones measured by Bouapao et al. [128]. However, the last authors reported two maxima at 110°C and 130°C corresponding to the different crystalline forms of PLA, the well-ordered α and less-ordered α' , whereas Zhang reports only one maximum at 120°C. Since no measurement was made between 110°C and 130°C, it is not possible to assess the presence of two maxima. Unlike the overall crystallization rate, the radial growth rate of spherulites increases with temperature. At 90°C, the growth rate is slower due to re-

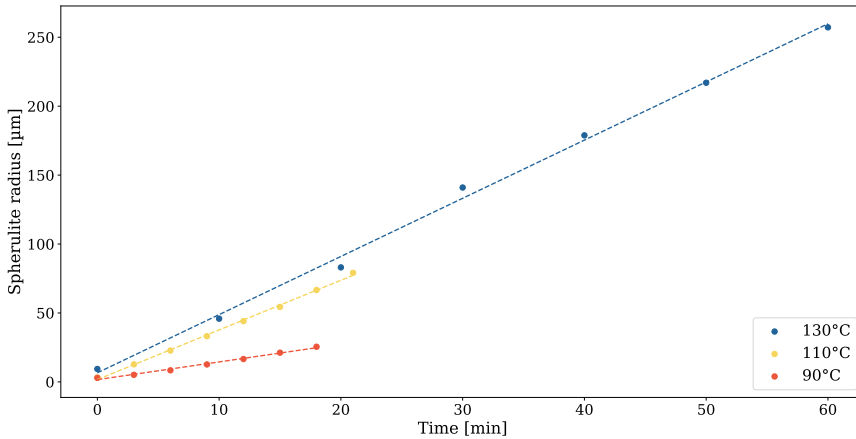


Fig. 1.4 Spherulite radial growth rate of PLA at different isothermal crystallization temperatures, extracted from POM images.

duced chain mobility, but the high nucleation density compensates for this, leading to a rapid overall crystallization rate. At 110°C, the growth rate is higher because the temperature provides optimal chain mobility while still maintaining sufficient thermodynamic driving force for crystallization. At 130°C, although the growth rate of individual spherulites is the highest, the overall crystallization process is slower due to the significantly reduced nucleation density.

POM analysis has revealed how the interplay between nucleation density and spherulite growth rate shapes the crystallization behavior of PLA. At 90°C, the extremely high nucleation density leads to the rapid formation of numerous small spherulites that quickly fill the sample volume. This compensates for the slower growth rate, resulting in a fast overall crystallization process. Conversely, at 130°C, the low nucleation density results in fewer but larger spherulites, leading to slower overall crystallization despite higher individual growth rates. The intermediate temperature of 110°C represents an optimal balance between nucleation density and growth rate, resulting in large spherulites and complete crystallization within 21 minutes.

From this section, it has been demonstrated that PLA crystallization is highly dependent on T_{hold} . An optimal crystallization temperature was identified between 100°C and 110°C, where the crystallization rate is maxi-

mized, combining moderate nucleation with rapid spherulite growth. At temperatures below 80°C or above 130°C, crystallization is either partial or absent due to insufficient or excessive molecular mobility. POM analysis of the spherulites reveals that nucleation density decreases with increasing temperature, while the growth rate increases almost linearly in this small temperature range.

The relationship between temperature, nucleation density and spherulitic growth rate highlights the importance of balancing these parameters to achieve specific crystalline morphologies in PLA/PEG blends. This balance is essential for regulating phase separation driven by PLA crystallization and directing PEG localization within the blend, which ultimately defines the porosity obtained after extraction.

1.2 Crystallization of neat PEG

Although PEG is ultimately used as a sacrificial material to induce porosity after extraction, it is still crucial to understand how PEG interacts with PLA within the blend and the effects this interaction has on the overall material structure and properties. Therefore, the crystallization of neat PEG needs to be studied.

1.2.1 Thermal characteristics of PEG

To assess the thermal behavior of different PEG samples, conventional DSC analysis was performed. In Figure 1.5 (left), the DSC cooling curves are shown. The sharp exothermic peaks demonstrate the rapid crystallization of PEG during cooling at 10°C/min. The well-defined nature of these peaks suggests that PEG crystallizes readily as the temperature reaches T_c , with the entire crystallization process occurring almost simultaneously. The crystallization temperatures on cooling at 10°C/min for PEG are 45°C, 34°C, and 42°C for molar masses of 3K, 100K, and 1M, respectively.

In Figure 1.5 (right) presents the DSC second heating curves of PEG samples after the cooling presented previously, showing the melting transitions of PEG crystals. For all PEGs, the melting peaks are sharp and well-defined, indicating a certain uniformity in the crystal structures. The melting temperatures for PEG 3K, 100K, and 1M are 74°C, 66°C, and 69°C, respectively.

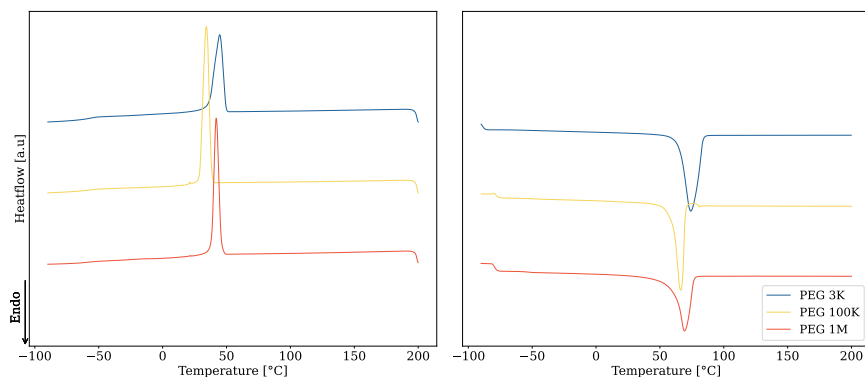


Fig. 1.5 DSC cooling curves from melt (left) and the subsequent 2nd heating curves (right) of PEG with molar masses of 3K, 100K and 1M, both at 10°C/min. The curves are displaced vertically for clarity.

The PEG samples were used as-is, without any prior thermal treatment.

The effect of molar mass on the melting temperature is influenced by two major factors. The first factor is chain mobility: shorter chains exhibit higher mobility, which positively impacts crystallization by allowing chains to align more easily and form crystals. The second factor is the concentration of chain ends: shorter chains result in a higher concentration of chain ends, which hinders crystallization as they act as defects within the crystals, leading to less perfect structures and a reduced melting point. The interplay between chain mobility and chain ends is apparent in the DSC results, as the crystallization temperature and melting temperature for the intermediate PEG100K are lower compared to those of PEG3K and PEG1M.

Also, due to the fast crystallization of PEG during cooling, isothermal crystallization at different temperatures is not feasible by DSC. Crystallization completes before reaching the desired isothermal temperature, underscoring the rapid crystallization kinetics of PEG.

Similar to PLA, fDSC was used to achieve rapid temperature changes that prevent the crystallization of PEG. As the PEG crystallizes much faster than PLA, it is important to define the suitable cooling rate that prevents reorganization prior to the isothermal crystallization. Figure 1.6 (left) presents the fDSC heating curves of PEG3K following cooling at speeds ranging from -4000°C/s to -1°C/s (which is still six times faster than in conventional

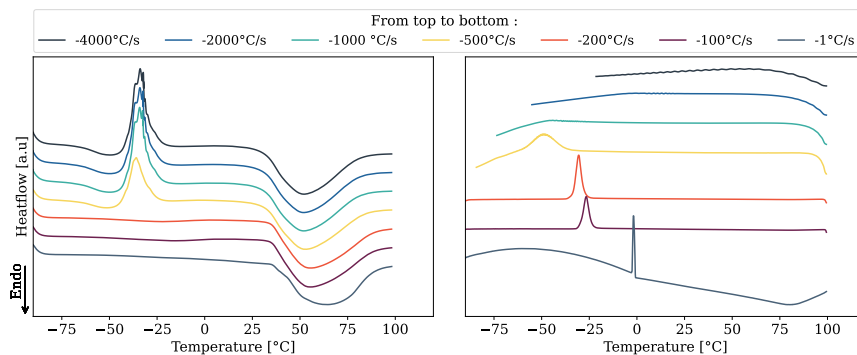


Fig. 1.6 fDSC heating curves (left) of PEG3K at constant 1000°C/s heating rate following the cooling curves (right) at different cooling rates. The curves are displaced vertically for clarity.

DSC). It appears that PEG undergoes cold crystallization upon heating at -34°C when cooled at -500°C/s or faster. However, when the cooling rate reaches -200°C/s or less, no cold crystallization is observed, indicating that PEG completely crystallized during cooling. It is also worth noting that the T_g of PEG, appearing at -59°C, is visible just before the cold crystallization.

To facilitate visualization, the cooling curves with the different cooling rates are shown in the right panel of Figure 1.6. In these curves, clear crystallization peaks can be seen for cooling rates below -500°C/s. At higher cooling rates, no crystallization peak is observed. At -500°C/s, a slight crystallization peak is still visible, indicating that PEG is capable of partially crystallizing at this cooling rate. This is further evidenced by the smaller cold crystallization observed during the subsequent heating curve. Based on these results, a minimum cooling rate of -1000°C/s is necessary to completely prevent crystallization of PEG during cooling. It is important to note that, due to the challenge of cooling the samples, the machine encounters difficulties in accurately tracking measurements at cooling rates of -500°C and higher. However, this does not affect the results discussed above. The large shoulder appearing before the peak for the -1°C/s cooling rate, is due to an artefact and will not be discussed.

When comparing the left and right graphs, it is evident that during constant heating, PEG consistently cold-crystallizes at -34°C. In contrast, the crystallization temperature during cooling varies significantly with the cooling rate, ranging from -50°C at -500°C/s to 0°C at -1°C/s, and even up

to 40°C at 10°C/min, as observed in the conventional DSC results. However, despite the variation in crystallization temperatures and whether crystallization occurred during cooling or heating, the melting temperature of the crystals remains practically unchanged.

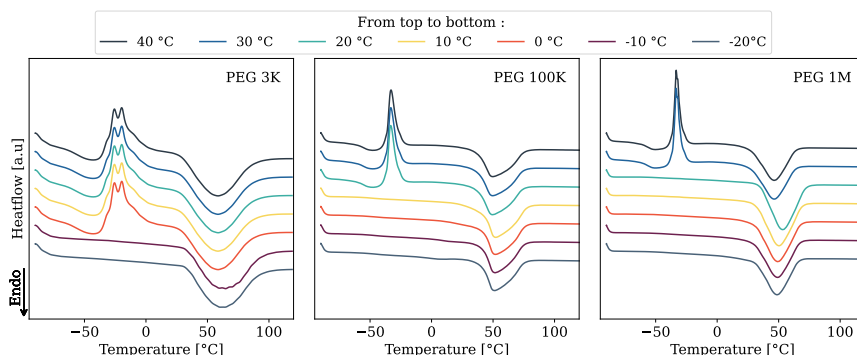


Fig. 1.7 fDSC heating curves of PEG 3K, 100K and 1M, after isothermal crystallization at the indicated temperatures for 10s. The curves are displaced vertically for clarity.

By using a cooling rate of $-1000^{\circ}\text{C}/\text{s}$, it is possible to induce isothermal crystallization of PEG at different crystallization temperatures. Figure 1.7 presents the heating curves of PEG after isotherms at temperatures ranging from 40°C to -20°C. The behavior across the three PEG samples is fairly similar. At higher temperatures, where T_{hold} is close to the melting point of PEG, the curves show the glass transition, followed by cold crystallization, and finally the melting of these crystals. At lower temperatures, however, PEG is able to crystallize during the isotherms, eliminating the occurrence of cold crystallization upon subsequent heating. Additionally, a threshold temperature exists for each PEG molar mass, below which PEG can crystallize during the isotherm. This threshold temperature increases with the PEG molar mass. PEG 3K starts crystallizing at -10°C, PEG 100K at 10°C, and PEG 1M at 20°C, indicating that longer PEG chains require higher temperatures to initiate isothermal crystallization.

In more detail, at higher T_{hold} , the melting occurs at 59°C, 50°C, and 46°C for PEG 3K, 100K, and 1M, respectively. T_g is similar across all samples, occurring at -59°C. Cold crystallization is observed at -33°C for PEG 100K and PEG 1M, while PEG 3K shows two cold crystallization peaks at -20°C

and -26°C . At lower T_{hold} , only the melting peak is present, occurring at 61°C , 51°C , and ranging between 53°C and 49°C for PEG 3K, 100K, and 1M, respectively. The appearance of two crystallization peaks for short PEG chains can be attributed to chain folding during crystallization, leading to the formation of crystals with different lamellar thicknesses and, consequently, different crystallization temperatures. Chain folding refers to the phenomenon by which polymer chains, too long to be fully extended in a single crystal, fold back on themselves. The lamellar thickness depends on the number of folds: crystals with fewer folds are thicker and generally exhibit higher thermal stability, while crystals with more folds are thinner and crystallize at lower temperatures. This structural variability is more pronounced for short chains, as differences in the number of folds significantly affect the relative crystal thickness. For higher-molecular-weight PEGs, the much longer chains lead to a more averaged folding behavior, which reduces the likelihood of observing multiple distinct crystallization peaks [129].

After the DSC analysis, the effect of chain ends and the molar mass of PEG were both identified as competing factors influencing the melting temperature. In the case of fDSC, PEG has less time to crystallize during the isotherm, leading to crystal growth that is predominantly influenced by chain length and mobility, rather than the presence of chain ends, which act as defects. This is evidenced by the observed decrease in melting temperature and the increase in threshold temperature as PEG molar mass increases. These results are important for understanding the crystallization behavior of PEG in blends, where it will be mixed with amorphous PLA chains or confined between PLA crystals.

1.3 Crystallization of PLA/PEG blends

Unlike the crystallization of neat polymers, crystallization within blends is influenced by the interactions between the constituent polymers, which affects both the degree of crystallinity and the phase separation behavior. For PLA/PEG blends, the crystallization of PLA can be significantly influenced by the miscibility and mobility of PEG [75, 74]. When both polymers are in the liquid phase, high miscibility may hinder PLA crystallization by a dilution effect, while low miscibility promotes phase separation, allowing larger

crystalline domains to form. When PLA begins to crystallize, PEG remains in a liquid state, allowing its chains to retain high mobility. Therefore, PEG can be expelled out of the growing spherulites. Despite being highly mobile, PEG chains can act as impurities by disrupting crystal formation, reducing crystal size, and potentially creating defects, thus strongly affecting the crystallization behavior of PLA. Understanding the PLA's crystallization mechanisms in these blends is crucial for controlling the distribution of PEG and the crystalline domains which directly impacts the microstructure, an essential factor for designing materials with tailored porosity.

1.3.1 Thermal characteristics of PLA/PEG blends

1.3.1.1 Effect of blends composition

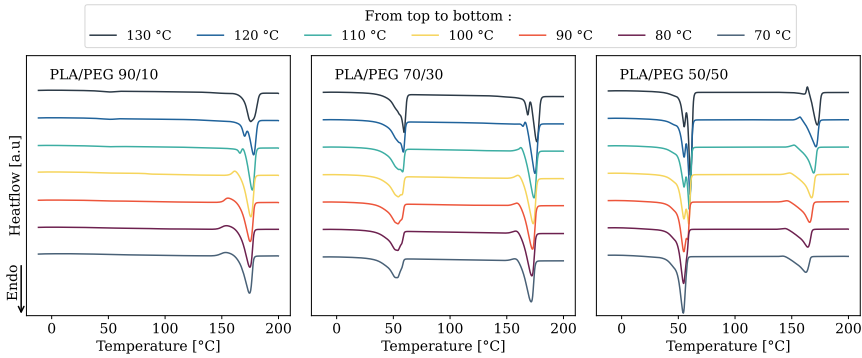


Fig. 1.8 DSC heating curves of PLA/PEG3K with compositions of 90/10 (left), 70/30 (center) and 50/50 (right), after isothermal crystallization at the indicated temperatures for 20min. The curves are displaced vertically for clarity.

To understand the effect of the composition, blends with 10%, 30% and 50% wt. PEG were prepared. This allows to see the behavior of PLA/PEG blends in the presence of low amount of PEG (90/10 blends), medium amount (70/30) and large amount (50/50). It is worth noting that phase separation occurs between PLA and PEG when the PEG concentration reaches the miscibility threshold. In the literature, this threshold is reported to vary from 10% wt. [65] to 50% wt. [77] but is most often situated around 30% wt. [74, 79, 119]. To ensure good mixing of the blends, they were dissolved in chloroform to obtain an homogeneous solution, then the

solvent was evaporated and the blends were dried before analysis. The isothermal crystallisation of PLA into the blends were investigated by DSC.

Figure 1.8 represents the DSC heating curves after isothermal crystallization at the indicated temperatures for 20 min. For each composition, the overall shapes of the curves are very similar to each other. However, some small changes can be noticed.

For the PLA/PEG 90/10 blend (left panel) only one melting peak is visible, corresponding to the PLA melting peak around 175°C. The values of the melting peaks are summarized in Table 1.3. At higher isothermal crystallization temperatures, two crystallization peaks are observed: a smaller one followed by a larger one, indicating the presence of two types of crystals. Typically, when two peaks are in close proximity, the crystals are of the same type, with the difference arising from some crystals being slightly less perfect, resulting in lower melting temperatures. The intensity of the smaller melting peak diminishes as the temperature decreases. Its disappearance coincides with the emergence of an exothermic reorganization peak, which, as previously observed for pure PLA (see Figure 1.1), appears just before the main melting peak. Interestingly, no direct trace of crystallized PEG is visible on the DSC curves. However, when comparing these curves with those for pure PLA, it clearly appears that in the PLA/PEG 90/10 blend, PLA is able to crystallize at all temperatures, even 130°C and 70°C, which was not the case for pure PLA.

For the 70/30 composition (center panel), the PLA is also able to crystallize at all temperatures, although its melting point is slightly lower compared to the 90/10 composition. Once again, at higher T_{hold} , two peaks of melting appears for PLA with the appearance of the reorganization peak corresponding to the disappearance of the small melting peak. Additionally, the melting peak of PEG around 60°C is now visible, indicating that PEG forms PEG-rich regions large enough to allow its crystallization. However, the broadness of the PEG melting peak suggests that the PEG crystals are substantially less perfect in the blends than when growing in pure PEG.

For the 50/50 composition (right panel), the melting peaks of PLA and PEG remain distinct. While the melting temperature of PEG is more constant than in the 70/30 blends, two melting peaks appear. The melting temperatures of PLA are slightly lower compared to the 70/30 composition and decrease further with decreasing T_{hold} . The peak shapes become asymmetrical, with a pronounced shoulder appearing. Additionally, reorganization occurs at all temperatures, with a more pronounced effect observed at higher T_{hold} . Due to the higher proportion of PEG in the sample, the

relative size of the PLA peak is smaller compared to the PEG peak, as there is simply less PLA present in the blend.

Table 1.3 Characteristic temperatures of PLA/PEG blends with the compositions 90/10, 70/30 and 50/50 extracted from DSC curves.

	T_{hold}	130°C	120°C	110°C	100°C	90°C	80°C	70°C
90/10	$T_{m,PLA}$ [°C]	176	178	177	176	175	175	174
	$T_{m,PEG}$ [°C]	-	-	-	-	-	-	-
70/30	$T_{m,PLA}$ [°C]	177	175	174	173	173	172	172
	$T_{m,PEG}$ [°C]	60	59	58	54	54	54	53
50/50	$T_{m,PLA}$ [°C]	172	171	169	168	166	164	163
	$T_{m,PEG}$ [°C]	61	60	60	59	55	55	55

From these figures, it is evident that the addition of PEG to PLA has a plasticizing effect. It facilitates PLA crystallization, making it possible over a wider range of temperatures. On one hand, the presence of PEG increases the mobility of PLA chains and may also increase the number of nucleation sites, since the impurities in PEG could act as a nucleating agent. On the other hand, the crystals formed are slightly thinner, as indicated by the reduction in PLA melting temperature. The more PEG is added to the blend, the more PEG surrounds the forming crystals, hindering their growth. This effect is particularly evident by the presence of reorganization peaks for all the T_{hold} and the broader melting peaks of PLA in the 50/50 blends, indicating the formation of a wider range of crystal sizes.

Another notable observation from these graphs is the absence of a PEG melting peak in the 90/10 composition, indicating a broad distribution of PEG within the PLA matrix. In this composition, the PEG-rich regions, if they exist, are too small to allow PEG crystallization, likely due to PEG being diluted within the amorphous phase of PLA or within the PLA spherulites. However, beyond 30% PEG-rich regions become sufficiently large to enable crystallization. This behavior already gives an indication of the partial miscibility between PLA and PEG, where a portion of PEG becomes trapped within the PLA amorphous phase in the PLA spherulites, preventing crystallization, while another portion segregates to form larger PEG-rich regions capable of crystallizing. These results are in good agreement with those of Younes and Goa where phase separation occurring at 30% wt. was also observed [74, 119].

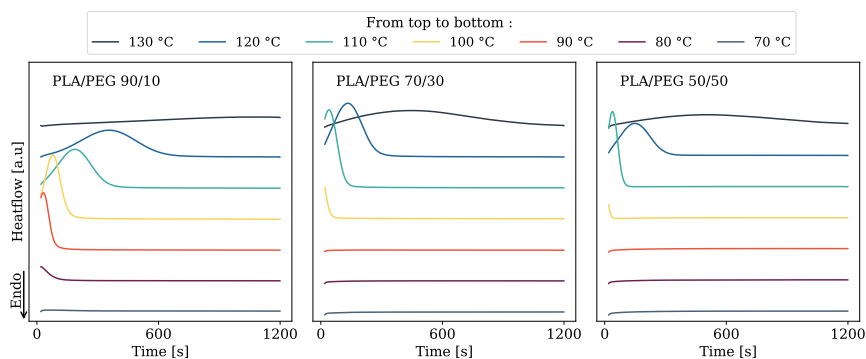


Fig. 1.9 DSC curves of PLA/PEG3K with compositions of 90/10 (left), 70/30 (center) and 50/50 (right), **during** isothermal crystallization at the indicated temperatures for 20min. The curves are displaced vertically for clarity.

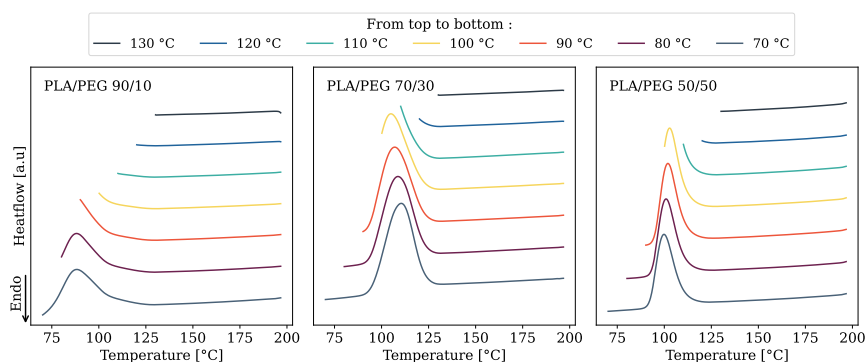


Fig. 1.10 DSC cooling curves of PLA/PEG3K with compositions of 90/10 (left), 70/30 (center) and 50/50 (right), **before** isothermal crystallization at the indicated temperatures for 20min. The curves are displaced vertically for clarity.

To better understand the crystallization of PLA in the blends, the DSC curves during the isotherms were recorded and are presented in Figure 1.9. In those curves, exothermic peaks of crystallization appear. However, the crystallization occurs very rapidly, to the extent that PLA begins to crystallize during the cooling phase before reaching the isothermal tempera-

ture. This is evidenced by the appearance of partial peaks at the start of the isotherm. Interestingly, the occurrence of reorganization prior to the melting of PLA crystals corresponds to isotherms where crystallization had already initiated during the cooling phase. Also, for the 90/10 composition, PLA crystallizes faster compared to pure PLA, as indicated by the leftward shift of the crystallization peaks. This effect is even more pronounced for the 70/30 and 50/50 blends, where only samples crystallized at 110°C or higher show crystallization during the isotherm. The absence of crystallization peak during the isotherms means that the crystallization already occurred during the cooling.

To complement these observations, the cooling curves recorded prior to the isotherms are shown in Figure 1.10. In these graphs, the onset of the crystallization peaks during cooling corresponds to the "tail" of the peaks observed during the isotherms. Moreover, in the 70/30 and 50/50 blends, PLA crystallizes at higher temperatures ($T_c \approx 105^\circ\text{C}$) than in the 90/10 blend ($T_c \approx 90^\circ\text{C}$) even though the T_m are the same.

1.3.1.2 Effect of PEG molar mass

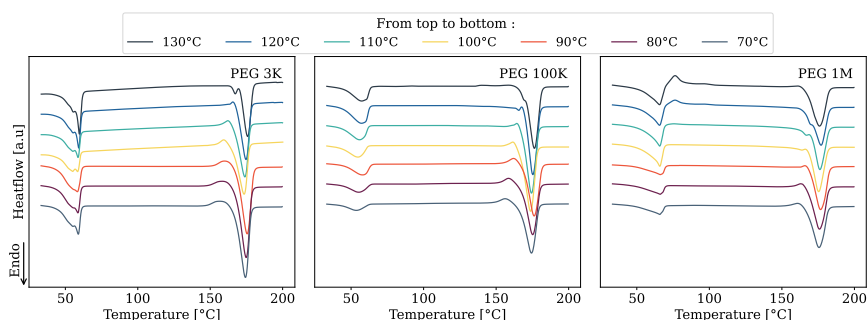


Fig. 1.11 DSC heating curves of PLA/PEG 70/30 with PEG molar masses of 3K (left), 100K (center) and 1M (right) after isothermal crystallization at the indicated temperatures for 10 min. The curves are displaced vertically for clarity.

The effect of PEG molar mass on PLA melting temperature in the 70/30 blends is minimal. As shown in Figure 1.11, each molar mass exhibits an initial endothermic peak corresponding to the melting of PEG crystals, followed by the melting peak of PLA crystals. Similar to the curves in Figure 1.8, PLA shows two crystallization peaks at higher T_{hold} , while exothermic

reorganization peaks appear at lower T_{hold} . The melting temperature of PLA remains constant at 175°C across all compositions and T_{hold} values, indicating negligible influence of PEG molar mass. Notably, PLA is able to crystallize at all T_{hold} values in these blends, unlike pure PLA. However, this behavior appears to be driven more by the blend composition than by PEG molar mass.

Interestingly, the melting point of PEG varies with its molar mass. The T_m values are 59°C, 56°C, and 66°C for PEG 3K, 100K, and 1M, respectively lower than the melting points of pure PEG at 74°C, 66°C, and 69°C (from DSC results of Figure 1.5). This reduction in PEG melting temperature supports the idea of good miscibility between PLA and PEG, as their interactions significantly influence each other's crystallization behavior. In contrast, an immiscible blend would show distinct, independent behaviors for each component.

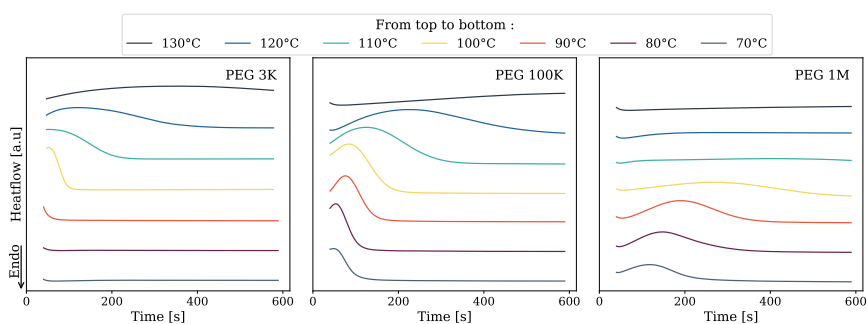


Fig. 1.12 DSC curves of PLA/PEG 70/30 with PEG molar masses of 3K (left), 100K (center) and 1M (right) during isothermal crystallization at the indicated temperatures.

Although the PEG has a limited effect on the melting temperature of PLA, it significantly influences PLA crystallization behavior. The isothermal curves in Figure 1.12 reveal that the PLA crystallization peaks occur at different times, with a clear shift to the right for blends containing PEG of higher molar mass, indicating longer crystallization times. In blends with PEG 3K, PLA crystallizes rapidly during the isothermal step at higher T_{hold} and progressively during cooling as T_{hold} decreases. While the cooling phase before T_{hold} is not shown, partial crystallization peaks confirm that PLA crystallized during this stage, as discussed previously. As PEG molar

mass increases, PLA primarily crystallizes during the isothermal step, with some crystallization still occurring during cooling, particularly at lower T_{hold} . For PEG 1M, PLA no longer crystallizes during the isothermal step at T_{hold} above 110°C but instead crystallizes during the cooling afterwards. Below this threshold, PLA crystallizes exclusively during the isothermal step.

These findings demonstrate the significant role of PEG molar mass in the crystallization rate of PLA. Lower molar mass PEG enables faster PLA crystallization due to reduced melt viscosity. Shorter PEG chains enhance PLA chain mobility, amplifying the plasticizing effect.

Although DSC provides valuable qualitative insights into crystallization behavior, it is limited for quantitative analysis due to its relatively slow cooling rate and the potential for reorganization before the isotherms. Since the crystallization spans both the cooling and isothermal segments of the DSC, it is challenging to perform an in-depth analysis of these curves, particularly regarding $t_{c1/2}$, which provides insights into the crystallization rate. For a more detailed analysis of the crystallization rate, the radial growth rate of spherulites can be computed with POM. The overall crystallization rate could then be estimated by combining the nucleation density and the radial growth rate. Additionally, to capture the "true" behavior of the PLA/PEG blends at the desired crystallization temperatures, fDSC is required to prevent any possible rearrangement during the experiments. This step is essential for establishing the phase diagram of PLA/PEG blends.

1.3.1.3 Effect of PEG on PLA crystal type

After DSC analyses, the blend composition has proven to be a key factor influencing the crystallization of PLA. In the presence of PEG, PLA can crystallize over a broader temperature range, and its melting temperature also changes depending on the amount of PEG in the blend. This raises the question of whether the addition of PEG leads to the formation of different types of PLA crystals. To address this, X-ray diffraction (XRD) experiments were conducted on various samples. Each sample was melted at 200°C between two glass slides and then cooled to 110°C for 1 hour, after which they were cooled to room temperature overnight. The corrected XRD results (see Section 1.3.5 for the correction method) for these samples are presented in Figure 1.13.

For pure PLA, a broad characteristic peak is observed at $s = 1.867 \text{ nm}^{-1}$

and a smaller one at $s = 2.135 \text{ nm}^{-1}$. For pure PEG, two broad peaks are located at $s = 2.152 \text{ nm}^{-1}$ and $s = 2.631 \text{ nm}^{-1}$. There are, therefore, very close diffraction peaks for PLA and PEG, at ca. 2.14 nm^{-1} , which cannot be used to discriminate PLA from PEG. However, it is possible to distinguish PLA from PEG based on the other peaks. Consequently, $s = 1.867 \text{ nm}^{-1}$ is taken as the characteristic peak for PLA, while $s = 2.631 \text{ nm}^{-1}$ is used for PEG. This distinction allows the separation of PEG and PLA spectra, which will be further elaborated in a subsequent section.

The results clearly show an increase in the PEG peak intensity with an increasing PEG content in the blend. When examining the characteristic peaks, it is also evident that the PLA spectrum remains unchanged, demonstrating that all the crystals formed are identical. One final noteworthy observation concerns the 90/10 blend, where the PEG signal is very weak or even absent. This can be explained in two ways: first, the signal is much weaker and therefore harder to detect, and second, as previously observed in the DSC results, PEG is unable to crystallize at such low concentrations due to its high dispersion in the amorphous phase of PLA into the spherulites.

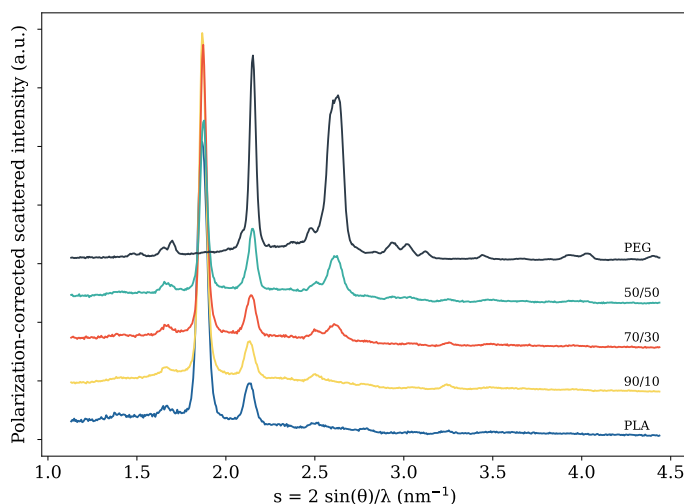


Fig. 1.13 XRD spectrum of PLA/PEG blends of composition 100/0 (pure PLA), 90/10, 70/30, 50/50 and 0/100 (pure PEG) of samples crystallized at 110°C for one hour then cooled to room temperature. The curves are shifted vertically for clarity.

1.3.2 Morphology of PLA/PEG blends after crystallization

1.3.2.1 Effect of blend composition

Understanding the morphological evolution of PLA/PEG blends requires an analysis of their spherulitic structures under different compositions and crystallization conditions. In Figure 1.14, POM images illustrate the different morphologies of spherulites obtained from PLA/PEG3K blends with compositions of 90/10, 70/30, and 50/50, each crystallized at 90°C, 110°C, and 130°C. According to the literature, the miscibility threshold between PLA and PEG is generally reported to lie around 30 wt% PEG [65, 77, 78, 79, 80]. Based on this, three compositions were selected: 90/10, representing a blend below the threshold; 70/30, corresponding to the vicinity of the threshold; and 50/50, clearly exceeding it.

As seen for PLA in the section 1.1.2, crystallization temperature significantly impacts the nucleation density and spherulite size. Examining the images from Figure 1.14 top to bottom reveals that increasing the crystallization temperature reduces the nucleation density, leading to larger spherulites. Those results are well in line with what was expected regarding the change in T_{hold} . However, for the PLA/PEG3K 50/50 blend, the PLA morphology stands out, as it forms large homogeneous spherulites even at 90°C.

In addition to temperature, the presence of PEG into the blend is another factor defining the spherulitic morphology. Observing the images from left to right highlights that at low PEG content, the spherulites are similar to those of pure PLA. However, as the PEG content increases, banded spherulites begin to appear. These bands are characteristic of twisting in PLA crystals caused by the presence of PEG [78, 127]. Within the amorphous phase near the PLA crystal growth front, PEG induces stresses that disrupt the parallel packing of PLA lamellae. This stress leads to a gradual twisting of the lamellae, creating the banded spherulite structure. This results in crystals in which an optical axis is alternately perpendicular (white) and parallel (black) relative to the orientation of the electric field of polarized light, leading to the formation of banded spherulites. The regularity of these bands reflects the homogeneous distribution of PEG within the PLA matrix. The width of the bands is influenced by T_{hold} , with higher temperatures resulting in wider bands [130].

It is noteworthy that even for compositions as high as 50/50, no amor-

phous regions or distinct spherulitic morphologies suggest the presence of PEG-rich zones between or inside spherulites. This indicates that PEG is well-distributed within the amorphous PLA phase and in the interlamellar or interfibrillar regions of PLA spherulites.

The observed morphologies also reflect changes in nucleation density, which depends on both temperature and blend composition. As explained in the section 2.1 of the State of the Art, the number of nucleation sites is represented by a bell shape curves that peaks between T_g and T_m , with the maximum situated below 90°C as the number of nucleation sites decreases with temperature (see Figure 1.16 left). Therefore, increasing PEG content shifts T_g to lower temperatures due to its plasticizing effect, which also reduces the nucleation site density. However, high PEG content dilutes PLA, making it less likely to reach the critical concentration needed for nucleation site formation. This explains why, at 90°C, the 50/50 blend exhibits large spherulites.

1.3.2.2 Effect of PEG molar mass

The effect of PEG molar mass on PLA crystallization in 70/30 blends is illustrated in Figure 1.15, which compares samples containing PEG 3K, 100K, and 1M. For all three PEG molar masses, banded spherulites are observed. However, the band periodicity varies slightly with molar mass: closer bands are observed for lower molar mass PEG, while more spaced bands appear for higher molar mass PEG.

Molar mass also influences the number of nucleation sites, as a greater number of spherulites are visible in samples with higher molar mass PEG. This can be attributed to the longer PEG chains, which promote heterogeneous nucleation and lead to increased spherulite formation.

Interestingly, PEG molar mass does not fundamentally alter the morphology of PLA crystals. Despite the significantly higher viscosity and reduced chain mobility of PEG 1M compared to PEG 3K, no evidence of PEG-rich regions, such as amorphous voids or accumulations at the edges of the spherulites, is observed. This suggests that PEG remains well mixed with PLA, even at very high molar masses.

To complement the analysis of spherulitic morphologies, examining the spherulite growth rates under similar crystallization conditions provides further insights into the effects of temperature and composition. The successive POM images allowed for the measurement of spherulite size as a

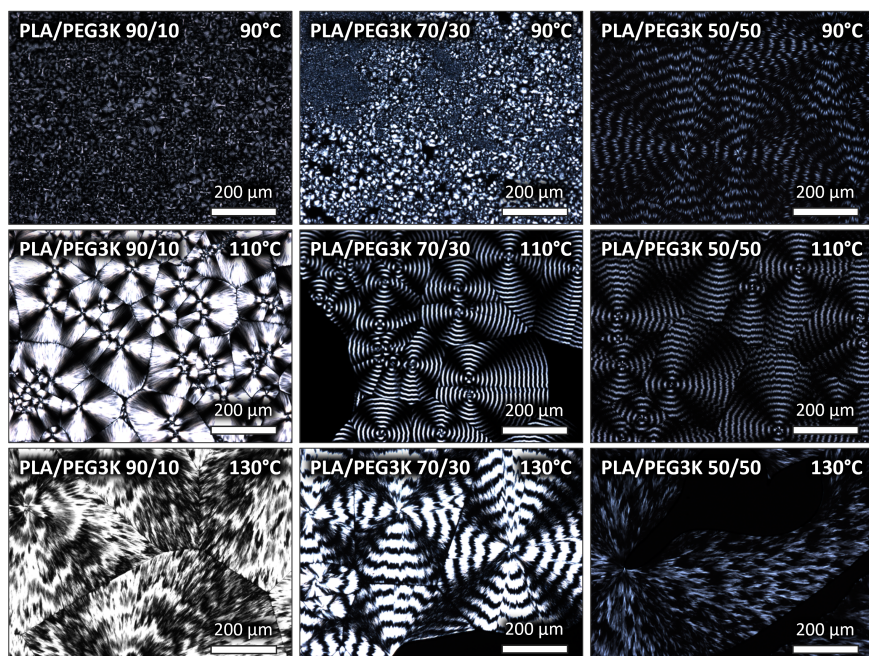


Fig. 1.14 Spherulitic morphologies of PLA/PEG3K blends observed by POM with compositions, 90/10 (left), 70/30 (center) and 50/50 (right) crystallized at 90°C (top), 110°C (middle) and 130°C (bottom).

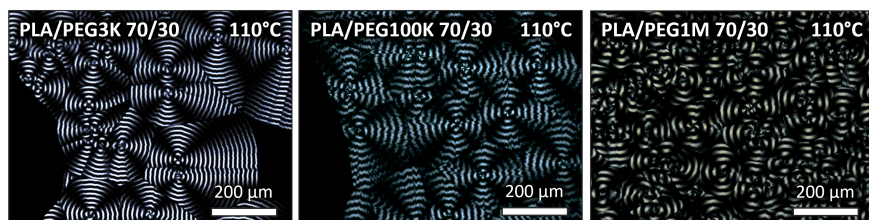


Fig. 1.15 Spherulitic morphologies of PLA/PEG 70/30 blends observed by POM with PEG molar mass of 3K (left), 100K (center) and 1M (right) crystallized at 110°C.

function of crystallization time. These measurements were used to evaluate the linear relationship between growth and time. The slopes of the resulting lines, representing the radial growth rate for each sample, were determined and are presented in Figure 1.16, with the effect of composition on growth

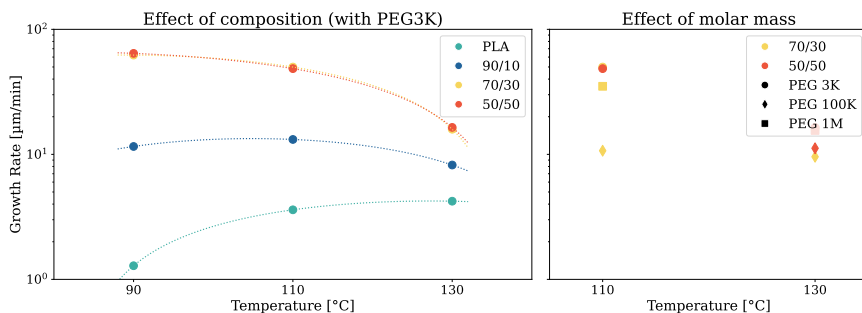


Fig. 1.16 Radial spherulitic growth rate of PLA/PEG blends during isotherms at 90°C, 110°C and 130°C. The effect of composition with PLA/PEG3K blends 90/10, 70/30 and 50/50 is shown on the left. The effect of PEG molar mass is shown on the right with PEG molar masses of 3K, 100K and 1M.

shown on the left panel for blends of 90/10, 70/30, and 50/50 with PEG3K. The PLA spherulite growth rate is relatively slow and slightly increases with temperature, as previously discussed in the PLA section. Generally, the addition of PEG accelerates spherulite growth due to its plasticizing effect, which enhances chain mobility. Consequently, the 90/10 blends show slightly higher growth rates, while the 70/30 and 50/50 blends exhibit significantly higher rates. Furthermore, the maximum growth rate shifts to lower temperatures, consistent with lower T_g for PLA/PEG blends following the addition of PEG. For pure PLA, the maximum peak is not clearly visible, but can be deduced to be around 130°C or slightly higher. In the 90/10 blend, the peak is evident at 110°C, whereas in the 70/30 and 50/50 blends, it shifts to approximately 90°C or lower. The similar behavior of 70/30 and 50/50 blends suggests a balance between the plasticizing effect of PEG, which increases growth rate, and the reduced PLA concentration near the growth front, which makes crystallization more challenging. These opposing effects seem to balance in the 70/30 and 50/50 blends at the tested crystallization temperatures.

Beyond composition and temperature, the molar mass of PEG introduces additional factors affecting spherulite growth, particularly through its impact on blend viscosity. The effect of PEG molar mass was also investigated and is presented in Figure 1.16 (right), comparing blends of PLA/PEG3K (identical to those in the left figure) with blends containing PEG100K and

PEG1M. As expected, blends with higher-molar-mass PEG show reduced spherulitic growth rates due to increased viscosity. This effect is more pronounced at lower T_{hold} , where viscosity is higher. Interestingly, in blends with PEG100K, growth rates are the lowest at both 110°C and 130°C and particularly at 110°C, which is quite surprising. The effect of PEG molar mass on the growth rate of PLA spherulites was not thoroughly studied in the literature. However, Zhang conducted an experiment involving bilayer films, where a pure PEG film was cast onto a pure PLA film. At the interface of these two layers, a mixed PLA/PEG region formed due to the diffusion of PEG chains. In this system, Zhang observed that the molar mass of PEG significantly influenced the crystallization rate of PLA spherulites. A lower PEG molar mass results in a higher radial growth rate of PLA spherulites [127].

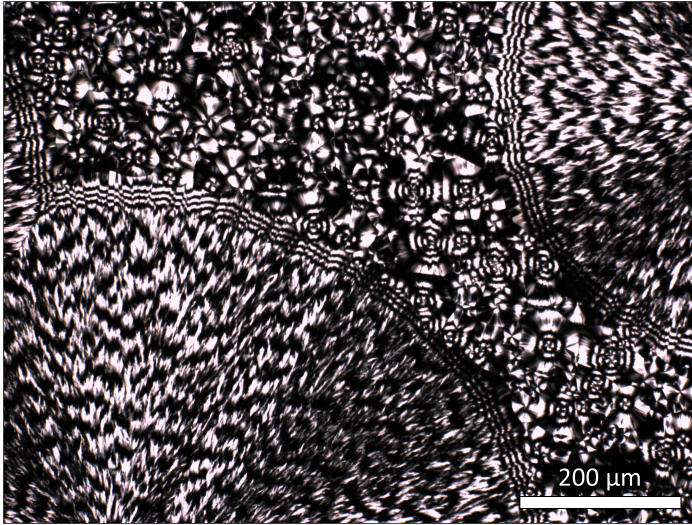


Fig. 1.17 POM image at room temperature of PLA/PEG3K 50/50 crystallized at 130°C. Two large banded spherulites can be seen in both corners surrounded by a ribbon of thinner bands. This large spherulites grew during the isotherm at 130°C. Between the two large spherulites, smaller spherulites grew during the uncontrolled cooling to room temperature.

Although PEG is not directly visible in Figure 1.17, the image offers valuable insights into the morphological evolution of the PLA/PEG3K 50/50 system during crystallization. The sample was crystallized isothermally

at 130°C for 70 minutes, then cooled to room temperature under ambient conditions. In the peripheral regions of the image, large banded spherulites are clearly observed; these developed during the isothermal step and are consistent in size and morphology with those presented in Figure 1.14. In contrast, the central area is populated by numerous smaller spherulites formed during the uncontrolled cooling phase. These display a variety of textures, including narrower band spacing, which is characteristic of crystallization at lower temperatures — as previously demonstrated.

A particularly noteworthy feature is the ribbon-like region that encircles the large spherulites. This zone exhibits finer banding than the interior of the isothermal spherulites, and its morphology closely resembles that of the small spherulites formed during the cooling phase. This observation strongly suggests that the ribbon crystallized under similar thermal conditions, i.e., during the uncontrolled non-isothermal cooling. Furthermore, the reduction in band spacing observed in this region is consistent with the trend shown in Figure 1.14, where spherulitic banding becomes progressively finer as the crystallization temperature decreases.

While the formation of these finer-banded structures can be adequately explained by temperature effects alone, the possibility of local PEG accumulation at the spherulite growth front — leading to subtle compositional variations — cannot be entirely excluded. This question will be further examined in the next chapter, which is dedicated to a detailed investigation of the phase behavior and spatial distribution of PEG within the PLA matrix.

1.3.3 Conclusions

The study of PLA/PEG blends reveals that the concentration and molar mass of PEG play a significant role on the crystallization behavior, spherulitic morphology, and phase distribution within the blends. At low PEG content, such as 10%, PEG acts as a plasticizer that enhances chain mobility and increases the nucleation density, facilitating PLA crystallization over a broader temperature range. However, PEG remains dispersed within the amorphous PLA phase, which prevents its own crystallization. As the PEG concentration increases to 30% and 50%, PEG-rich regions begin to form, allowing PEG to crystallize. However, these regions could only be identified through the presence of PEG crystals by XRD and DSC, not in POM. They are therefore relatively large compared to the crystals

but still remain quite small, below the micrometer range. At higher concentrations, the presence of PEG reduces the size and melting temperature of PLA crystals, as it surrounds the PLA crystals and hinders their growth. This behavior suggests partial miscibility between PLA and PEG, where PEG is distributed both within the amorphous PLA phase and as separate PEG-rich zones.

The effect of PEG molar mass is equally notable. Lower PEG molar mass, such as PEG 3K, amplifies the plasticizing effect, accelerating PLA crystallization and spherulitic growth rates. In contrast, higher PEG molar mass, such as PEG 1M, increases the blend viscosity, which slows down PLA crystallization, particularly at lower temperatures. Despite these differences, PEG remains well mixed with PLA, with no evidence of large amorphous or phase-separated zones, highlighting a good miscibility between the two polymers.

The location of PEG within the blends further emphasizes its role in phase separation during PLA crystallization. A portion of the PEG is trapped inside the growing spherulites of PLA, as shown by the presence of uniform bands, while another part of the PEG accumulates at the growth front of PLA spherulites, inducing the formation of a PEG-rich ribbons. These features are particularly visible after uncontrolled cooling, where the expulsion of PEG during crystallization demonstrates its mobility and interaction with the growing PLA crystals.

Overall, the results suggest partial miscibility between PLA and PEG. At low PEG concentrations, PEG dissolves into the PLA amorphous phase inside PLA spherulites, while at higher concentrations, it segregates into PEG-rich domains that are able to crystallize. The observed reduction in PEG melting temperature within the blends compared to pure PEG shows that its crystallization is made more difficult due to its high proximity with PLA crystals.

These results are particularly relevant to the phase diagram of PLA/PEG blends. However, the current evidence remains insufficient to determine the precise localization of PEG within the blends. Therefore, the next chapter will focus on constructing the phase diagram of PLA/PEG blends. A thorough understanding of this diagram will provide insights into PEG distribution and, consequently, enable better control over the resulting porosity after PEG extraction.

2

Phase separation between PLA and PEG

2.1 Miscibility and crystallization of PLA/PEG blends

In the previous chapter, the crystallization behavior of PLA and PEG was analyzed using conventional DSC. However, it was observed that studying the thermal behavior of the blend below the crystallization temperature of PLA was challenging due to the progressive phase transformation occurring during cooling. To overcome this limitation, the same approach was applied using flash DSC, that enables extremely high heating and cooling rates, set at 1000 K/s. This method allows the sample to be frozen at a specific temperature, preventing any structural rearrangement before analysis. By examining the thermal behavior upon heating, it is then possible to understand the state of the blend at the target temperature. Based on these different thermal regimes, a phase diagram of the PLA/PEG system can be elaborated.

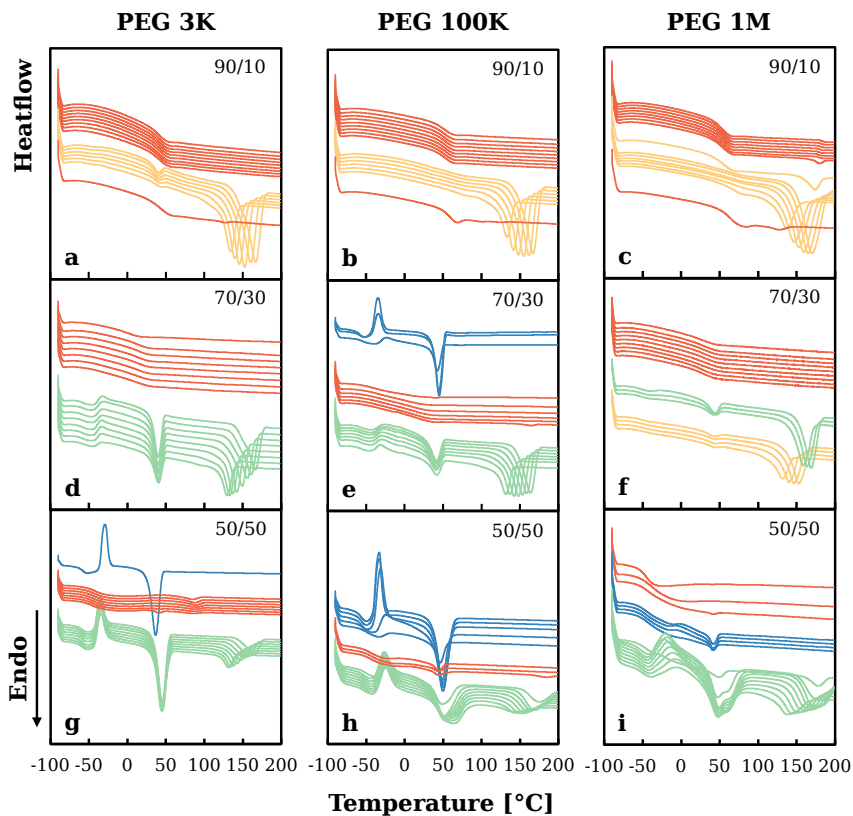


Fig. 2.1 fDSC second heating curves for PLA/PEG samples 90/10 (a, b, c), 70/30 (d, e, g) and 50/50 (g, h, i) with T_{hold} varying from 200°C to 50°C by steps of 10°C from top to bottom in a panel (the curves have been shifted vertically for clarity). The PEG molar mass is 3K (a, d, g), 100K (b, e, h) and 1M (c, f, i). The colors are used to identify different categories of behavior at T_{hold} . Type I (red): miscible amorphous blend with no visible melting peak. Type II (yellow): liquid-solid phase separation driven by PLA crystallization without PEG crystallization during the isothermal treatment. Type III (green): liquid-solid phase separation driven by PLA crystallization with PEG crystallization during isothermal treatment. Type IV (blue): liquid-liquid phase separation.

2.1.1 Analysis of liquid-solid and liquid-liquid phase separation

The fDSC procedure described previously in the section 1.3.1 from Materials and Methods was applied for analyzing all PLA/PEG blend samples of

three compositions (90/10, 70/30, and 50/50) with PEG of three different molar mass (3K, 100K, and 1M). Note that the procedure is the same as the DSC method explained in the section 1.3 with faster heating and cooling rates. The isothermal duration was reduced to 5 minutes, as thermodynamic equilibrium was reached within this timeframe for low temperatures (90–110°C) and high temperatures (180°C), as evidenced by the fDSC curves presented in Annex 1, although these data are not discussed in detail in the present section. The curves presented in Figure 2.1 illustrate the second heating curves for samples 90/10 (a, b, c), 70/30 (d, e, f) and 50/50 (g, h, i) with PEG molar masses of 3K (a, d, g), 100K (b, e, h) and 1M (c, f, i). In each graph of Figure 2.1, T_{hold} varies from 200°C (upper curve) to 50°C (lower curve), with an increment of 10°C.

Since the main objective is to interpret the interactions between PLA and PEG within the blend, the principal trends observed in the fDSC curves are examined, with colors for the traces used to help the reader sort the different samples in different categories of behavior. As previously mentioned, due to the complexity of determining the mass of the sample, any quantitative analysis is difficult. Therefore, only a qualitative study is conducted, which is sufficient to evaluate the miscibility of PLA and PEG.

In Figure 2.1a, b, and c, the behavior of the 90/10 blends exhibits a consistent pattern independently of the PEG molar mass. Notably, a single T_g is observed for equilibration temperatures T_{hold} between 200 and 120 °C (red curves), whose temperature location should correspond to the one of a miscible amorphous blend according to Fox's equation [72]. The width of the specific heat jump at T_g is not large, which is indicative of the homogeneity of the blend composition at T_{hold} . For T_{hold} values between 110 and 60°C (yellow curves), PLA undergoes crystallization during isothermal equilibration at T_{hold} ; as a result, a high temperature endotherm is detected upon heating, corresponding to the melting of PLA crystals, with a melting temperature ($T_{m,PLA}$) decreasing as T_{hold} decreases (yellow curves). Additionally, a small melting endotherm of PEG crystals is observed slightly before 50°C for the lower PEG molar mass, indicating that PEG crystallized at least partially during cooling after PLA crystallization at T_{hold} , owing to its accumulation in PEG-rich regions due to segregation during PLA crystallization. The downward shift of $T_{m,PLA}$ as T_{hold} decreases is due to PLA crystallizing at different T_{hold} temperatures, resulting in the selection of a lower average lamellar thickness and consequently lower melting

temperature. This is qualitatively in accordance with the Hoffman-Weeks relationship [52], although the possible depression of the melting temperature due to the presence of PEG in the amorphous regions surrounding PLA crystals might complicate the picture. Finally, at a T_{hold} of 50°C, the temperature is insufficient to allow PLA crystallization, resulting in the observation of a single T_g , similar to the isotherms at higher temperatures; these fDSC traces are actually more complex but will not be discussed further.

PLA/PEG 70/30 blends (Figure 2.1d, e, and f) exhibit a more diverse behavior depending on the PEG molar mass. For PEG 3K (Figure 2.1d), a single T_g is observed under isothermal equilibration conditions ranging from 200 to 130°C (red curves), again testifying for the homogeneity of the amorphous blend at these temperatures; nevertheless, the width of the glass transition increases, suggesting less locally-homogeneous blends. Furthermore, several thermal transitions occur during the heating following isothermal equilibration between 120 and 50°C (green curves). These transitions appear in the following sequence: T_g of PEG ($T_{g,PEG}$), cold crystallization of PEG ($T_{cc,PEG}$), PEG melting ($T_{m,PEG}$), and $T_{m,PLA}$. The presence of well-defined PEG transitions proves that PEG accumulates in PEG-rich regions during the equilibration of the blend at T_{hold} , due to liquid-solid phase separation induced by PLA crystallization; the invariance of $T_{m,PEG}$ with T_{hold} results from it crystallizing upon heating from PEG-rich regions in the fDSC. Again, the downward shift of $T_{m,PLA}$ as T_{hold} decreases is due to PLA crystallizing at different T_{hold} temperatures as for the yellow curves in panels a-c. Of note, $T_{g,PLA}$ is not detected on these curves, which can be attributed to two factors: reduced specific heat jump due to PLA crystallinity and overlap with the PEG melting peak in the same temperature range.

For PEG 100K (Figure 2.1e), a supplementary behavior appears when T_{hold} exceeds 170°C (blue curves). In this T_{hold} range, the PLA melting peak is not visible, indicating that PLA remains in an amorphous state when held above its melting temperature, which is hardly surprising. However, the observation of PEG thermal transitions, which become less prominent as temperature decreases, is indicative of a liquid-liquid phase separation in this T_{hold} range, that is stronger at higher temperatures, suggesting the presence of a lower critical solution temperature (LCST) for this specific blend. Below 170°C, the behavior observed for the blend of lower PEG molar mass is recovered.

For PEG 1M (Figure 2.1f), the same behavior as for the blend with the PEG of lower molar mass is observed for T_{hold} above 90°C. From this point on, however, the thermal transitions of PEG become barely perceptible (yellow curves), which indicates that PEG cannot crystallize as readily in the PLA-crystallized blend. This must be due to larger constraints set on the PEG chains, either resulting from segregation in regions of much lower size still interacting strongly with PLA rich regions, or from incomplete segregation. Both phenomena are favored by the increased viscosity of the PEG chains of high molar mass, in qualitative agreement with predictions made in the seminal work of Keith and Padden [70].

PLA/PEG 50/50 blends (Figure 2.1g, h, and i) exhibit the same categories of behavior as blends of lower PEG content, but for different isothermal equilibration temperatures. For PEG 3K and PEG 100K, the behavior of 50/50 and 70/30 blends is very similar, with a region of liquid-liquid phase separation at high temperatures (blue curves, not detected at lower PEG contents), homogenous composition at intermediate equilibration temperature (red curves) and liquid-solid phase separation due to PLA crystallization at lower equilibration temperature (green curves). The T_g of the homogeneous blends are located at lower temperatures than in PLA-richer blends, again in qualitative accordance with Fox's equation. In liquid-solid phase-separated blends, the T_g of PEG is also lower than for other samples, which indicates that PEG accumulates in PLA-poorer regions upon segregation. Likewise, the melting enthalpy of PEG is now significantly larger than the one of PLA, due to the higher PEG content. Other minimal differences are observed in the behaviors of the 70/30 and 50/50 blends for PEG 100K when comparing Figure 2.1e and h. Although the three distinct behaviors remain consistent, the transition between them occurs at lower temperatures; for instance, the transition between blue and red curves happens at 160°C for 50/50 blends and 180°C for 70/30 blends.

The most intriguing behavior is exhibited by the 50/50 blend with PEG 1 M (Figure 2.1i), for which a single sharp glass transition is observed at 200°C, indicating miscibility in the melt; however, as the equilibration temperature decreases, the T_g broadens considerably then the behavior of a liquid-liquid phase-separated blend emerges for T_{hold} between 170 and 140°C, before liquid-solid phase separation starts to appear (green curves). Such a behavior is typical for the existence of an upper critical solution temperature (UCST). Finally, in the low temperature region, two melting

endotherms are detected for PEG, suggestive of the possibility that PEG crystallized in two environments, one being associated to PEG-rich regions appearing due to partial liquid-liquid phase separation, the second resulting from liquid-solid phase separation in PLA-rich regions of the liquid-liquid phase separated morphology.

Summing up, four different types of behavior can be distinguished depending on equilibration temperature, blend composition and PEG molar mass: Type I (red curves) corresponding to homogeneous amorphous blends in which no crystallization occurs at T_{hold} . Type II (yellow curves), for which PLA crystallizes from a homogeneous amorphous mixture resulting in liquid-solid phase separation, while PEG does not (or hardly) crystallize owing to its small concentration or constraints set by nearby PLA crystals. Type III (green curves) for which both PLA and PEG crystallize, indicative of a liquid-solid phase separation from a homogeneous and in some case liquid-liquid phase-separated blend. Type IV (blue curves), for which only PEG crystallizes from PEG-rich regions created by a liquid-liquid phase separation process in the amorphous blend. To add to this complexity of behaviors, some curves exhibit hybrid states, straddling the boundaries of two distinct behaviors. Therefore, they could arguably be associated with a supplementary specific behavior. But more importantly, these hybrid curves show that the transition from one behavior to another one occurs progressively, without sudden or abrupt shifts.

Overall, the complexity of the phase diagram is astonishing, with the possible existence of two liquid-liquid phase separation processes (UCST and LCST) appearing depending on equilibration temperature and on PEG concentration and molar mass and a liquid-solid phase separation appearing afterwards.

Type I behavior is typical of a miscible blend where the $T_{g,blend}$ is located between the T_g of PLA (332.5 K for a high molar mass and slow cooling [131]) and the T_g of PEG (206 K for a high molar mass and slow cooling [132]). This indicates that PLA and PEG form a single liquid phase in these conditions. The glass transition of these blends at different compositions and for different molar masses are presented in Figure 2.2. As expected, when increasing the PEG content in the blend, $T_{g,blend}$ decreases significantly. The values of the glass transition temperature of a miscible blend can be estimated by Couchman's equation [73], using the values of specific heat

jump of the two polymers at T_g (38.96 J/mol/K [132] and 42.07 J/mol/K [131] for PEG and PLA, respectively); this equation is often simplified to give Fox's equation, which is valid when the glass transition temperatures and specific heat jumps at T_g are not too different. The $T_{g,blend}$ computed by Couchman's equation are 40°C for 90/10, 17°C for 70/30 and -9°C for 50/50. These values are only indicative, since chain end effects cannot be neglected for PEG 3K; furthermore, owing to the rapid cooling in the fDSC, kinetic effects could result in shifts of the glass transition by as much as 10 K. The $T_{g,blend}$ measured on non-crystallized blends (Figure 2.2) significantly differs from the expected theoretical value; at higher PEG contents, they are generally consistently lower than the theoretical values (represented by dotted lines in Figure 2.2). In addition to the effects mentioned above, local fluctuations of concentrations in the blends, which are indicated by the breadth of the specific heat jump at T_g , may also contribute to the discrepancy between expected and measured values.

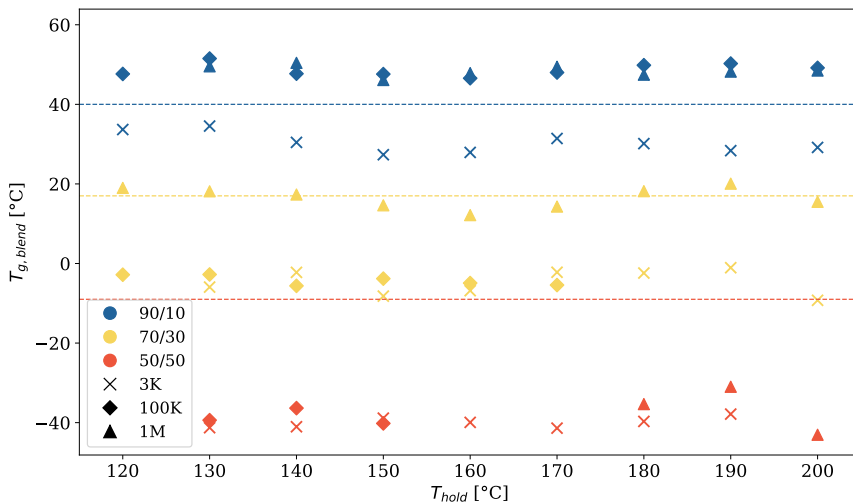


Fig. 2.2 T_{blend} from Type I curves in which only a single T_g is present, for non-crystallized PLA/PEG blends of 90/10 (blue), 70/30 (yellow), 50/50 (red) with PEG molar mass of 3K (×), 100K (◆) and 1M (▲), versus the equilibration temperature T_{hold} . Theoretical T_g derived from Couchman's equation are represented by dotted lines in the corresponding colors.

The T_g measured for the three 70/30 blends are also reported in Figure

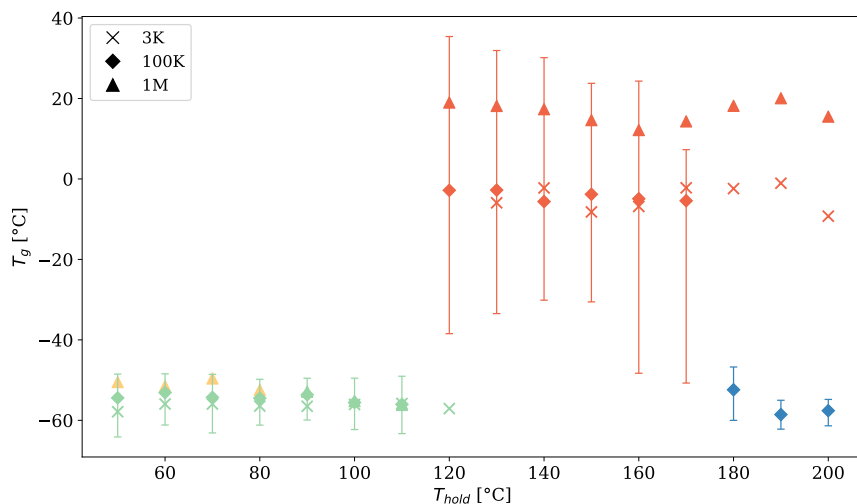


Fig. 2.3 T_g of PLA/PEG 70/30 blends depending on T_{hold} . The PEG molar masses are (x), 100K (◆) and 1M (▲). The different colors correspond to the different types of behaviors: type I (red), II (yellow), III (green) and IV (blue). Errors bars are only shown for PEG 100K for clarity and correspond to the temperature range between the onset and offset temperatures of the specific heat jump.

2.3. For the sake of clarity, the color code remains consistent with the different behaviors displayed in Figure 2.1. In the low and high T_{hold} ranges, only the glass transition of almost pure PEG is detected at ca. -50°C , due to liquid-solid (low T_{hold}) or liquid-liquid (high T_{hold}) phase separation with the formation of almost pure PEG regions. In the intermediate range of equilibration temperatures, a glass transition temperature of a miscible blend is obtained, indicating the formation of a homogeneous mixture of PLA and PEG, thus demonstrating miscibility. However, the onsets and offsets of the glass transition (represented by the lower and upper bars in Figure 2.3) indicate a relatively heterogeneous local concentration within the blends, as previously discussed. Given that the behavior across temperature ranges is consistent regardless of PEG molar mass, only the onset and the offset for PEG 100K are represented on the graph for more clarity.

Since crystallization occurs for types II, III and IV behaviors, it is interesting to investigate what happens in the blend when one polymer crystallizes

while the other remains in the liquid state. According to the simplified model of Keith and Paden [70], when a polymer crystallizes into spherulites from the melt in the presence of non-crystallizable impurities, these impurities are excluded from the crystals and form an impurity-rich layer. The thickness of this layer scales as $\delta = D/G$, in which D is the diffusion coefficient of impurities in the melt, and G represents the radial growth rate of the spherulites. Consequently, if D is large compared to G , a significant proportion of impurities is expelled from the spherulites, resulting in a large δ . Conversely, when G is large compared to D , the crystallization occurs too fast to expel all the impurities out of the spherulites. As a result, δ becomes small, and most impurities remain trapped within the spherulites, which can occur either inter-fibrillarly when impurities form rather pure channels located between stacks of crystalline lamellae (so-called fibrils), or inter-lamellarly when it accumulates in the amorphous interlamellar regions of the crystallizing polymer in coexistence with amorphous segments of this polymer (tie molecules, loose folds, sharp folds, dangling chain ends,...) [133]. When PLA crystallizes during the equilibration isotherms, PEG chains act as impurities. A proportion of them will thus be expelled inter-spherulitically while the remaining part will be trapped intra-spherulitically either in interfibrillar or interlamellar regions, depending on the D/G ratio. In Type II behavior (yellow curves), only PLA crystallizes with no PEG crystallization detected upon reheating. This behavior mainly appears for 90/10 blends in which the PEG concentration is low. The PEG-rich zones, resulting from the exclusion of PEG or its entrapment within the spherulites, are too small and/or not pure enough to allow PEG crystallization. This suggests that the liquid-solid phase separation triggered by PLA crystallization results in interlamellar segregation of PEG, or possibly interfibrillar segregation in very small pockets in the spherulitic microstructure of PLA. In Type III behavior (green curves), PLA crystallizes during the isothermal equilibration, whereas PEG crystallizes upon heating. During PLA crystallization at T_{hold} , PEG is thus expelled out of the growing PLA crystals (liquid-solid phase separation) and accumulates to form PEG-rich areas, either in interspherulitic or interfibrillar regions. This behavior appears for all 70/30 and 50/50 blends. At those concentrations, PEG thus forms pockets within the PLA crystalline microstructure, large enough to crystallize. Finally, for Type IV behavior (blue curves), only PEG crystallizes during heating after equilibration, as evidenced by the presence of its cold crystallization peak. This behavior is mostly observed at high T_{hold} indicating that during the isothermal treatment, PLA and PEG underwent liquid-liquid

phase separation.

It is important to note that Keith and Padden's theory aids in understanding the various behaviors observed in the blend. However, the fDSC curves alone do not provide a fully non-ambiguous evidence to determine the position of the PEG within the PLA. Another technique allowing observation of sample morphology is required. Results obtained by SEM will be presented in a subsequent section to support these hypotheses.

2.1.2 Complete phase diagrams of PLA/PEG

Based on the fDSC analysis described in the previous section, it is possible to draw temperature-concentration phase diagrams for the PLA/PEG blends of different PEG molar mass. These phase diagrams are presented in Figure 2.4 as color maps corresponding to the different behaviors of the blend, using the same color code as before. The phase diagram for PEG 3K is on the left, the one for PEG 100K is in the middle and the one for PEG 1M is on the right. In this figure, two regimes common to all three phase diagrams are discernible. For improved clarity, a small schematic has been included in the figure to illustrate the corresponding phase separation state for each behavior. These schematic representations are intended solely to aid visualization at this stage; their interpretation and relevance will be discussed in more detail in the following chapter.

For high temperatures above 120-140°C, PLA does not crystallize during equilibration (red and blue, corresponding to behavior types I and IV). In this temperature regime, PEG is miscible with PLA at low concentrations; a liquid-liquid phase separation appears at higher concentrations, with a LCST clearly visible. For the high molar mass PEG, however, a UCST also seems to exist at higher temperatures. For lower temperatures, liquid-solid phase separation happens following PLA crystallization, with large regions of pure PEG appearing above 30% PEG (behavior types II and III). Remarkably, PLA is capable of crystallizing at isotherms ranging from 120 to 60°C, down to ca. 10°C below its T_g . This plasticizing effect can be attributed to the presence of PEG, which increases chain mobility and reduces $T_{g,PLA}$ upon mixing, allowing crystallization at lower temperatures.

To achieve the desired porosity in the material, it is essential to cre-

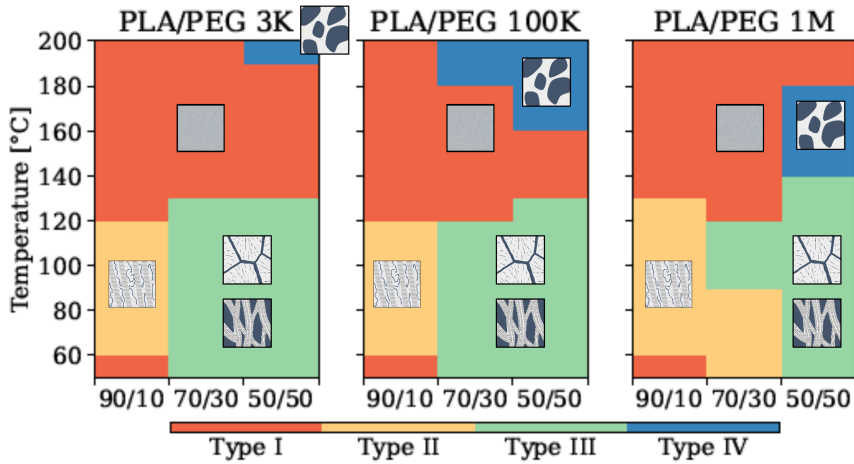


Fig. 2.4 Temperature-concentration phase diagrams of PLA/PEG blends based on the four types of behaviors obtained by fDSC for PEG 3K (left), PLA/PEG 100K (center), PLA/PEG 1M (right). Type I : Miscible blends. Type II : liquid-solid phase separation driven by PLA crystallization with PEG segregation in interlamellar PLLA/PEG regions. Type III : liquid-solid phase separation driven by PLA crystallization with PEG segregation in interspherulitic and/or interfibrillar regions. Type IV : liquid-liquid phase separation. For improved clarity, a small schematic has been included in the figure to illustrate the corresponding phase separation state for each behavior.

ate PEG-rich regions that can be selectively extracted. If such regions are absent, PEG chains will remain intimately mixed with PLA chains in the amorphous phase, making their removal challenging and resulting in insufficient porosity. Similarly, in the presence of liquid-liquid phase separation, it is very likely that the PEG-rich phases will be discontinuous, leading to potentially large but highly heterogeneous porosity, provided that the solvent can penetrate the PEG-rich regions and efficiently dissolve them. Furthermore, since liquid-liquid phase separation only occurs at elevated temperatures, it is practically difficult to cool the system fast enough to prevent phase homogenization upon temperature reduction.

For optimal porosity, the phase separation conditions should be chosen such that PEG-rich domains are both interconnected and homogeneously distributed throughout the material. In this regard, Type III behavior ap-

pears to be the most suitable. However, it is crucial to consider that, under this regime, PEG accumulates in interspherulitic, interfibrillar, and interlamellar regions. While the segregation of PEG in interspherulitic domains enhances porosity, it also compromises the structural integrity of the material, as the spherulites are no longer interconnected. Therefore, the objective is to maximize PEG capture in interfibrillar regions, where it forms sufficiently large PEG-rich areas while maintaining material cohesion.

These aspects will be explored in greater detail in the next chapter, which focuses on porosity analysis via SEM imaging.

2.1.3 Implications of the phase diagram on processing parameters

The phase diagrams established from fDSC experiments serve as predictive tools to anticipate the structural outcomes resulting from thermal processing of PLA/PEG blends. Since the ultimate objective is to fabricate 3D-printed objects, the material must first be extruded into filament and subsequently re-extruded during the printing process. To ensure proper mixing and avoid premature phase separation, the blend must be fully molten and located within the homogeneous region of the phase diagram during filament extrusion. During 3D printing, however, temperature control—particularly of the cooling rate—is limited on most commercially available printers. As a result, depending on the extrusion temperature and the bed temperature, the system may traverse different miscibility domains upon cooling, ranging from fully miscible amorphous phases to crystallization-induced phase separation. Adjusting the extrusion temperature allows positioning the material within a desired domain of the phase diagram prior to solidification, thereby influencing PEG distribution and the resulting porosity. Additionally, if the printed parts are quenched, thermal annealing can be performed to induce crystallization post-processing. However, in this case, crystallization will proceed from the solid state rather than from the melt. It is also important to note that at most annealing temperatures where PLA crystallizes efficiently, PEG remains in a liquid state, which promotes its mobility and potential redistribution during crystallization. Understanding these dynamic transitions is essential for tailoring both the microstructure and the porosity of the final printed objects.

3

Induced porosity in PLA/PEG materials by PEG extraction

The porosity of the final material is inherently linked to the phase behavior of PLA and PEG within the blend. Since PEG is the sacrificial phase responsible for generating porosity upon extraction, its distribution and connectivity prior to removal play an important role in determining the resulting pore architecture. Based on the findings of the previous chapter, the phase diagram of PLA/PEG has been established, allowing the identification of different phase separation behaviors. This understanding enables the selection of optimal conditions for inducing porosity in the material.

To effectively generate pores, the PEG-rich domains must be both sufficiently large and interconnected to ensure their complete and uniform dissolution. This requires selection of phase separation conditions that promote the formation of well-defined PEG-rich regions rather than a homogeneous amorphous mixture or a discontinuous liquid-liquid phase separation morphology. Type III behavior, driven by liquid-solid phase separation during PLA crystallization, is therefore particularly suitable. Additionally, PEG tends to segregate into specific regions of the microstructure, such as interspherulitic, interfibrillar, and interlamellar domains. The precise localization of PEG within these regions will strongly influence not

only the porosity but also the mechanical integrity of the material.

By selecting an appropriate solvent that efficiently dissolves PEG while remaining a nonsolvent for PLA, it is possible to selectively extract PEG without affecting the PLA matrix. The resulting porosity will then reflect the spatial arrangement of PEG prior to extraction.

This chapter will analyze the porosity of the PLA/PEG blends following PEG extraction, with a focus on correlating the observed pore morphology with the phase behavior discussed previously. SEM imaging will be used to assess the distribution, connectivity, and scale of the pores, providing further insight into the relationship between phase separation mechanisms and the resulting material architecture. Additionally, the efficiency of PEG extraction will be evaluated by quantifying the residual PEG content in the material using ^1H NMR analysis.

3.1 Extraction of PEG from the blends

Before analyzing porosity, it is essential to first examine the efficiency of PEG extraction. As previously discussed, achieving porosity requires the use of a solvent that selectively dissolves PEG without affecting PLA. In this context, water serves as an ideal candidate. The extraction method, detailed in the section 1.2.5 from the Materials and Methods, involves immersing the samples in distilled water for 24h, followed by drying before analysis. To assess the efficiency of the extraction process, different samples were prepared, including thin PLA/PEG 70/30 films with a thickness of approximately 100 μm for each PEG molar mass (3K, 100K, and 1M). Additionally, 3D-printed objects composed of PLA/PEG 70/30 blends with the same PEG molar masses were fabricated to evaluate the extraction efficiency in thicker materials, with a thickness of around 2 mm. The use of 3D printing also allows for verifying whether the extraction method remains effective even after the material has undergone shaping and processing.

After extraction and drying, the samples were dissolved in deuterated chloroform and analyzed by proton NMR. Figure 3.1 presents the characteristic peaks of PLA and PEG100K, along with the spectra of a PLA/PEG100K 70/30 film before and after extraction. The PEG spectrum displays a single peak at 3.64 ppm, corresponding to the four identical hydrogen atoms of

PEG. The PLA spectrum shows a quartet centered at 5.16 ppm and a doublet at 1.58 ppm, attributed to the H_α and the three identical hydrogen from the methyl group ($-CH_3$), respectively. Based on these peaks, the PEG mass fraction in each sample was determined by peak integration, as described in the Materials and Methods.

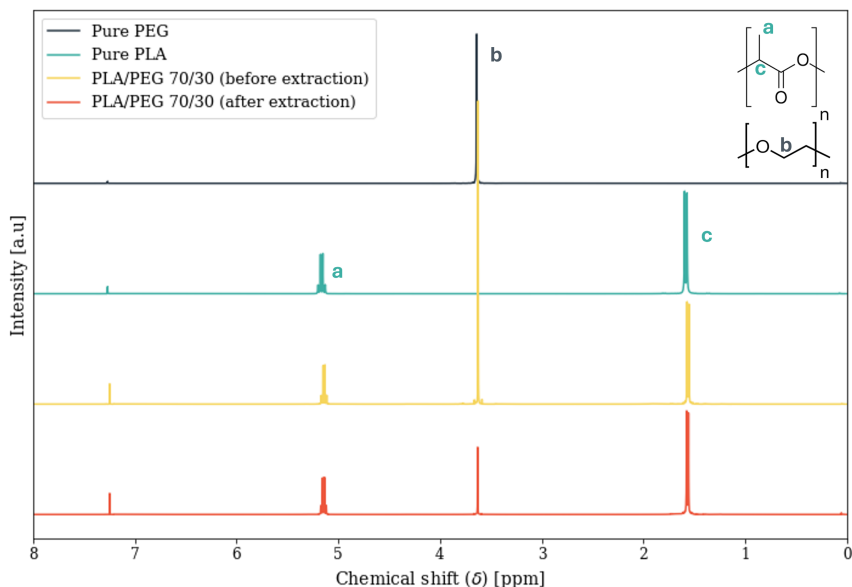


Fig. 3.1 NMR spectra of (from top to bottom) pure PEG, pure PLA, PLA/PEG100K 70/30 films before and after PEG extraction. The peak at 7.28 ppm corresponds the solvent ($CDCl_3$).

For the PLA/PEG100K 70/30 film shown in Figure 3.1, the PEG mass fraction before and after extraction was measured to be 28.7% and 8.2%, respectively. These values, along with those for other samples, are summarized in Table 3.1. Overall, a significant fraction of PEG (between 7 and 10%) remains in the samples, regardless of molar mass or sample thickness. However, PEG molar mass does influence the residual PEG content: higher molar mass PEG tends to be retained in slightly greater amounts. Although this difference is relatively small (only a few percent), it remains noteworthy.

As discussed in the previous chapter, during PLA crystallization, a fraction of PEG is incorporated into the amorphous phase of PLA. Due to chain entanglement between PLA and PEG, extracting PEG entirely from

Table 3.1 Values of peak integration computed from NMR spectra, with the corresponding calculated PEG weight fraction after PEG extraction. All samples were initially made with 30% wt. PEG of the mentioned molar mass. "Film" samples were produced by solvent casting and are considered as thinner objects. "3D" samples were produces by 3D-printing of PLA/PEG 70/30 filaments and are considered as thicker objects.

	$H_{PLA,\alpha}$	H_{PLA,CH_3}	H_{PEG,CH_2}	% _{wt} PEG
PLA/PEG100K 70/30 (before extraction)	1.05	3.18	2.77	28.7
Film 3K	2.05	5.95	1.00	6.9
Film 100K	1.74	5.24	1.02	8.2
Film 1M	1.08	3.12	0.80	10.2
3D 3K	2.02	5.88	1.10	7.7
3D 100K	1.77	5.88	1.10	8.7
3D 1M	1.08	0.79	3.13	10.1

these regions is challenging. This explains why higher molar mass PEG is more difficult to remove, as its longer chains become more entangled within the PLA matrix.

In contrast, PEG located in larger interfibrillar and interspherulitic regions is easily extracted. This is reflected in the fact that PEG retention does not depend on sample thickness. Indeed, as shown in Table 3.1, the proportion of residual PEG remains relatively constant whatever the size of the sample. This suggests effective solvent penetration and uniform PEG dissolution throughout the material.

Additionally, this observation implies a high degree of pore interconnectivity. However, one possibility remains: the residual PEG may be trapped in large, isolated regions that are not interconnected and therefore remain undissolved during extraction. This hypothesis will be further examined in the following section.

3.2 Microporosity induced in PLA/PEG films

3.2.1 Impact of the composition of PLA/PEG films on the resulting porosity

To assess the effect of the composition on the porosity, PLA/PEG3K blends of compositions 90/10, 70/30 and 50/50 were melted and quenched to 110°C, a temperature at which liquid-solid phase separation occurs due to the crystallization of PLA (types II and III, presented in Figure 2.4). The blends were held for 4 h before being quenched to room temperature to freeze the microstructure. Subsequently, PEG was extracted with the method described above, and the porous films were dried before analysis. To analyze the impact of the composition on the resulting sample morphology, the surfaces of the films were first observed by SEM, the images are presented in Figure 3.2.

In Figure 3.2a, white areas corresponding to the original location of the PEG before extraction are visible. These areas are relatively small and distributed throughout the material, in accordance with type-II behavior (no large PEG regions in the microstructure). With increasing PEG concentration within the blend, there is an accumulation of PEG at the PLA spherulite interfaces, along with larger PEG-rich regions within them, corresponding to type-III behavior. As discussed in the previous chapter, a proportion

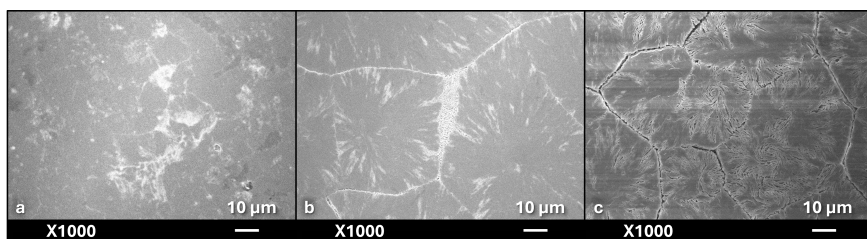


Fig. 3.2 SEM images of the surface of PLA/PEG3K films crystallized for 4 h at 110°C, after PEG extraction, revealing the effect of PEG content on the resulting porous morphology. The initial blend composition before extraction is 90/10 (a), 70/30 (b), and 50/50 (c).

of PEG is trapped within PLA spherulites, while another part is excluded, residing in the interspherulitic regions. This is precisely what is observed in Figure 3.2b,c for the 70/30 and 50/50 blends. Additionally, intraspherulitic PEG zones exhibit an elongated radial appearance, indicating their entrapment between lamellar stacks (fibrils). The 70/30 and 50/50 blends exhibit similar characteristics with these features becoming more pronounced with increasing PEG concentration. For the higher PEG content, accumulation of PEG in interspherulitic regions even leads to a spherulite disjunction and material decohesion.

To emphasize this effect, the cross-section of PLA/PEG 70/30 and 50/50 films is presented in Figure 3.3(a, c) and (b, d), respectively, for molar masses of 100K (a, b) and 1M (c, d). These films were crystallized at 110°C for 4 hours and subsequently extracted in water, as previously described. To obtain a clean fracture surface, the samples were immersed in liquid nitrogen and then fractured. In the case of the 70/30 blend, the cross-section reveals well-defined spherulites with smaller intraspherulitic porosity and good cohesion between them, resulting in a continuous film structure. With increasing PEG content, larger pores become visible within the spherulites, while significant PEG accumulation in the interspherulitic regions leads to spherulite decohesion. Consequently, after PEG extraction, the PLA/PEG 50/50 films exhibit pronounced brittleness.

This behavior is consistent with the findings of Kuterbekov [5], who demonstrated that when PLA is blended with PEG in a 30/70 ratio at 110°C, independent PLA spherulites form within the molten PEG. Therefore, approaching the 50/50 composition leads to less cohesive arrangement of spherulites. This explains the observed loss of cohesion and the increased

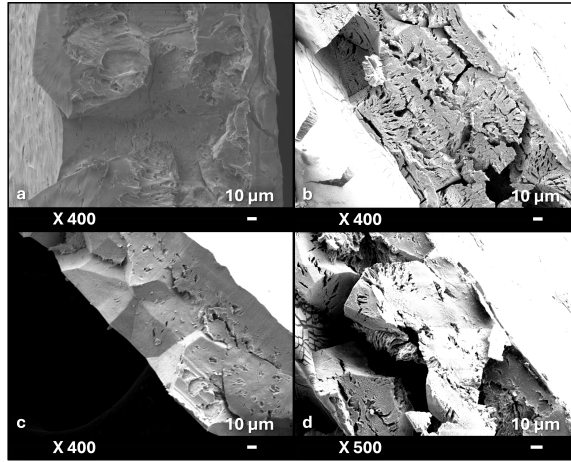


Fig. 3.3 SEM images of the cross-section of PLA/PEG films after PEG extraction, revealing internal porosity. The initial blend composition before extraction is 70/30 (a, c) and 50/50 (b, d), with PEG molar masses of 100K (a, b) and 1M (c, d).

brittleness of the 50/50 films after PEG extraction. Notably, the molar mass of PEG appears to have a negligible effect on these morphological features, as similar structural characteristics are observed for both 100K (a, b) and 1M PEG (b, d).

Based on these results, the 70/30 samples emerged as the most promising candidates for combining porosity and mechanical properties as 90/10 blends are not porous enough and 50/50 blends are too fragile. Therefore, all the further experiments were done on PLA/PEG 70/30 blends.

Comparing the images in Figures 3.2 and 3.3 reveals a significant difference between the surface and bulk morphologies of the samples. To illustrate this transition, Figure 3.4 presents a view from the surface to the edge of the film where the bulk can be seen, highlighting the resulting changes in porosity for a PLA/PEG100K 70/30 film.

In Figure 3.4a, the surface exhibits well-defined spherulites, delimited by a thin white boundary, along with large pores aligned with the growth direction of the spherulites corresponding to the previous presence of PEG before extraction. Despite their size, these pores are distributed rather heterogeneously. Moving towards the film edge (Figure 3.4b), the morphology

changes significantly, with a bulk structure characterized by smaller but more evenly distributed pores. A closer view of this transition zone (Figure 3.4c) reveals a fine porosity at the micron scale, with a relatively homogeneous distribution.

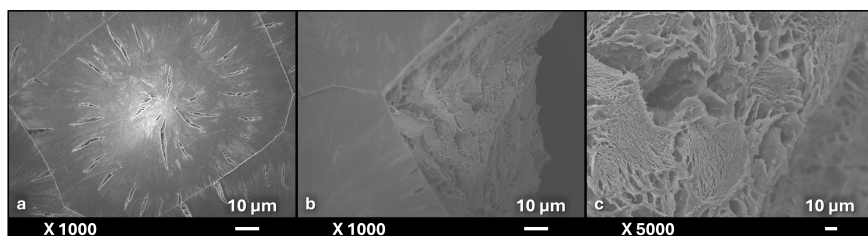


Fig. 3.4 SEM images of a PLA/PEG100K 70/30 film after PEG extraction, highlighting morphological variations at different locations: the surface (a), the transition zone at the edge (b), and the bulk of the cross-section (c).

This difference in morphology can be directly attributed to the film fabrication method. As detailed in Materials and Methods, the films are produced by melting and then crystallizing the material between the plates of a hot press. This process induces preferential crystallization at the surface, while in the bulk, spherulites can grow independently. During their growth, spherulites at the surface are constrained, causing them to flatten and limiting the formation of small-scale porosity. Consequently, PEG accumulates preferentially in certain areas rather than being uniformly distributed, leading to the formation of less pores at the surface but more evenly dispersed pores in the bulk.

Under standard crystallization conditions, i.e., without preferential surface crystallization, PEG becomes entrapped within PLA spherulites, forming small, uniformly distributed pores. This observation aligns well with the previously discussed phase diagram. Upon cooling from the melt to the PLA crystallization temperature, in this case 110°C, crystallization occurs from a homogeneous mixture, ensuring an even distribution of PLA and PEG. During PLA crystallization, a significant amount of PEG is present in the surrounding regions and is incorporated into the growing spherulites, leading to the formation of PEG-rich regions inside PLA spherulites which become small, homogeneously distributed pores after PEG extraction.

Notably, PEG accumulation in interspherulitic regions appears to be minimal, given the narrowness of these zones. This is particularly interest-

ing, as it suggests that most of the PEG is concentrated within interfibrillar regions. After extraction, this results in a porosity distributed throughout the material while avoiding the interfacial decohesion issues mentioned earlier. Since the amount of PEG dissolved in the amorphous PLA regions remains constant (between 7 and 10%), the limited PEG presence in interspherulitic zones maximizes its concentration in interfibrillar regions, thereby enhancing the overall porosity of the material.

3.2.2 Effect of PEG molar mass on the bulk porosity of PLA/PEG films

In order to analyse the bulk porosity, which is the primary focus, the porosity after PEG removal was thus studied over the cross-section of the film rather than on film surfaces. These images are presented in Figure 3.5, for PEG 3K (a, d), 100K (b, e), and 1M (c, f). As expected, all films showed the porosity associated with the extraction of larger PEG-rich regions. The top row samples (Figure 3.5a-c) display interspherulitic porosity vs the PEG molar mass; the interspherulitic porosity is stronger for the lower PEG molar masses. Due to its larger molar mass, PEG 1M is less readily expelled (smaller diffusion coefficient D) and tends to segregate predominantly in intraspherulitic regions. On the bottom row (Figure 3.5d-f), intraspherulitic porosity is depicted. A very similar open porosity is evident across all samples. The elongated appearance of pores is consistent with PEG entrapment during PLA crystallization. It is also noteworthy that pore sizes range from 0.5 to 1.5 μm as also found by Lai [117] that produced porous PLA/PEG films with a similar morphology. Although the pore size remains below 100 μm , the common threshold for cell migration [1], the presence of widespread porosity throughout the material can still promote the diffusion of nutrients, oxygen and other elements carried by biological fluids. These results indicate that in 70/30 blends, PEG accumulation in interspherulitic regions remains relatively limited but can be adjusted by reducing the PEG molar mass, which increases the proportion of PEG expelled from the spherulites. This can allow to change the interspherulitic porosity of the material at the expense of its mechanical properties. Therefore, trade-offs need to be made depending on the targeted applications.

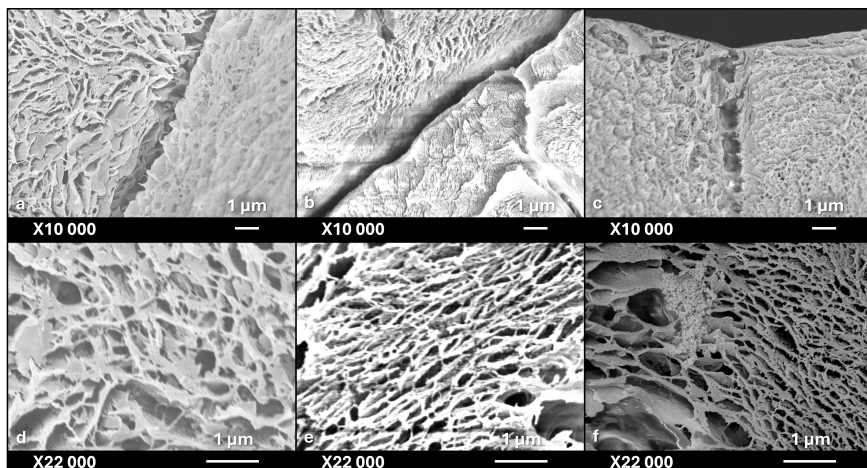


Fig. 3.5 SEM images of the bulk of PLA/PEG 70/30 films after PEG extraction, highlighting the influence of PEG molar mass on the porous structure. The PEG molar masses before extraction are 3K (a, e), 100K (b, d), and 1M (c, f). The top row illustrates interspherulitic porosity, while the bottom row highlights intraspherulitic porosity.

3.2.3 Predicting porosity in PLA/PEG blends based on phase diagram

Now that the creation of microporosity by PEG extraction has actually been observed, it is possible to correlate the SEM images with the established PLA/PEG phase diagram to determine the location of PEG in the PLA microstructure as a function of isotherm temperature. The different possible morphologies of the PLA/PEG blends are presented in Figure 3.6, where PEG is represented in blue and PLA in gray. In the high-temperature regime, the blend is in the liquid phase, where PEG and PLA form a homogeneous liquid (type I) resulting in a single phase (Figure 3.6 a), or form a liquid-liquid phase-separated mixture (type IV) with a PEG-rich phase and a PLA-rich phase (Figure 3.6 b). SEM images illustrating the binodal liquid-liquid phase separation were not included in the main text but are provided in Annex 1. However, in the low-temperature regime, the crystallization of PLA in the presence of liquid PEG needs to be considered using Keith and Padden's theory [70]. Therefore, when PLA crystallizes (type II and III) slowly (spherulitic radial growth G decreases), PEG has enough time to diffuse out of the spherulites, and the segregation spatial scale δ is

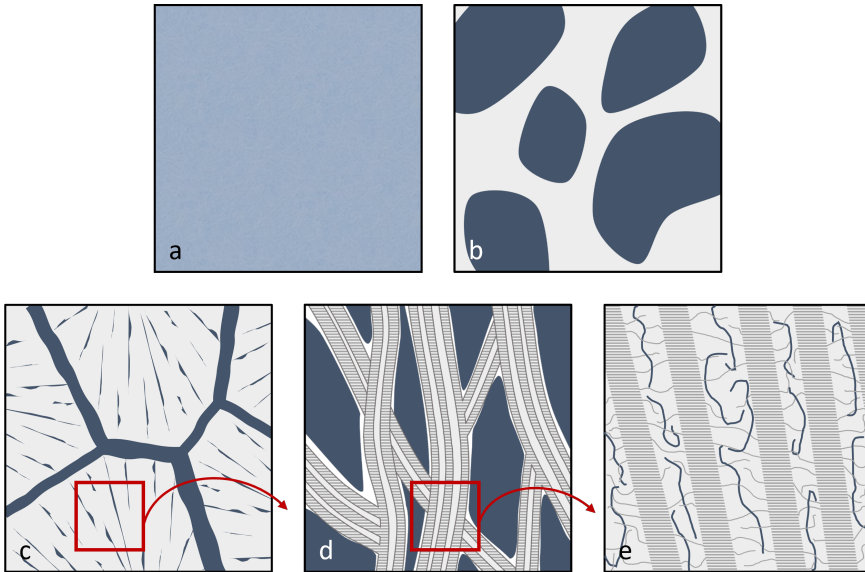


Fig. 3.6 Various positions of PEG (blue) mixed with PLA (gray). In the liquid phase: homogeneous blend (a) or heterogeneous blend (b) corresponding to red and blue regions of the phase diagram of Figure 2.4, respectively. In the solid phase, corresponding to yellow and green regions of the phase diagram: PEG located in interspherulitic regions (c), interfibrillar regions (d), and interlamellar regions (e). The proportion between the different types of PEG segregation depends on the concentration and molar mass of PEG, with lower molar masses and higher concentrations favoring interspherulitic and interfibrillar segregation.

large (Figure 3.6 c). However, if the crystallization rate G is larger than the diffusion speed, a larger proportion of PEG is trapped inside the spherulites either in interlamellar (Figure 3.6 e) or interfibrillar regions (Figure 3.6 d). In the case of interlamellar segregation, amorphous interlamellar regions exist in which the PLA and PEG chains are mixed; in this case, complete PEG extraction might be difficult and the porosity might be difficult to detect. Although the interlamellar PEG is not directly visible, its presence is confirmed by the NMR results after PEG extraction (see Table 3.1). Moreover, the hypothesis that large, closed PEG-rich regions remain in the sample can be ruled out, as none of the SEM images exhibit such a morphology.

Lastly, from the previously presented XRD resulted (Figure 1.13) the

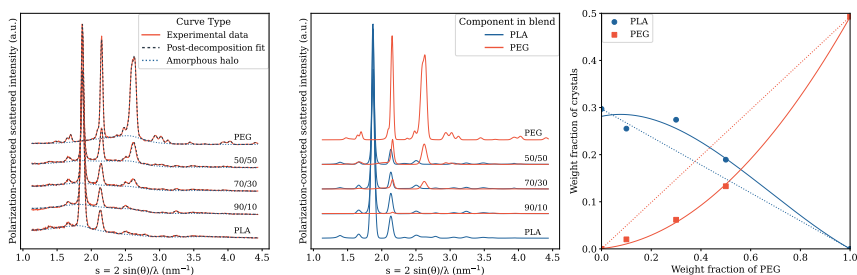


Fig. 3.7 Scattered intensity of PLA and PEG100K calculated from the decomposition of XRD spectra. The samples were melted then isothermally crystallized at 110°C. The left panel shows the experimental XRD data (solid red lines) along with the corresponding decomposition into amorphous halos (dotted blue lines) and the post-decomposition fitted curves (dashed black lines). The middle panel presents the scattered intensity of crystalline PLA (blue) and PEG (red) regions extracted from the decomposition. The right panel displays the mass fraction of crystalline PLA and crystalline PEG in the sample (solid lines), compared to the expected values based on the total PEG content (dotted lines).

peaks corresponding to crystallized PLA and PEG can be used to evaluate the fraction of PEG that undergoes crystallization within the PLA matrix. Consequently, the remaining non-crystallized PEG can be computed.

The scattering of the blends from Figure 1.13 was decomposed using a linear combination of the PEG and PLA amorphous halos plus a sum of crystalline peaks for which the shape, position and width were kept constant to the values found for the pure polymers. The amorphous halos and the post-decomposition fits are shown in Figure 3.7, left panel with dashed blue and dashed black lines, respectively. From the decomposition, the signal $I_c(s)$ of the crystalline PEG and PLA was obtained (Figure 3.7, middle panel).

The mass fraction of crystalline PEG and crystalline PLA in the samples was estimated by taking the ratio of the integral of $2\pi s^2 I_c(s)$ to the integral of $2\pi s^2 I(s)$, in which $I(s)$ is the total intensity scattered by the sample. These mass fractions are close to the mass crystallinity; however, due to the limited scattering range measured, they are not strictly equal to the mass crystallinity.

As Figure 3.7 (right panel) shows, the crystalline content in PLA relative to the total amount of PLA is slightly larger in the blends than expected

based on a simple linear rule of mixture (dotted blue line), showing that PLA crystallizes more in the blends, presumably due to plasticization by PEG. More interestingly, the crystalline content in PEG is significantly reduced in the blends by comparison to what could be expected based on PEG content (dotted red line). This indicates that a significant fraction of PEG is trapped in the semi-crystalline structure of the blend, and does not crystallize as if it was pure. Such a trapping can only occur in constrained regions such as interlamellar PLA regions; indeed, when PEG exists in almost pure composition in larger regions such as interfibrillar or interspherulitic regions, from which it can be extracted, nothing should oppose its crystallization. The difference between the red dotted line and the measured fraction of PEG crystals represent the fraction of PEG which is trapped and does not crystallize; it amounts to 29% of the PEG for blends comprising 10 and 30% PEG, and 23% of the PEG for the blend containing 50% PEG.

Therefore, if 29% of the PEG present in the 70/30 blend is trapped inside the amorphous phase of PLA, in total this corresponds to 9% wt. of PEG relative to the sample mass that does not crystallize. This is in accordance with the remaining trapped PEG measured by NMR after extraction.

3.2.4 3D images of PLA/PEG films

Although microporosity was observed in all previous samples, and the effective dissolution of PEG confirmed the formation of an interconnected pore network, obtaining a 3D visualization remains valuable. A 3D image allows for a better understanding of pore distribution throughout the material while also providing a quantitative assessment of porosity. To achieve this, Micro-CT scanning was used to image a PLA/PEG100K 70/30 film after PEG extraction. The resulting images are presented in Figure 3.8.

In Figure 3.8 (a), an overall view of the film is displayed, where PLA appears in gray and pores are shown in green. Examining the film surface reveals larger, elongated green areas that correspond to interspherulitic regions. Within individual spherulites, smaller PEG-rich zones are visible, radiating outward from their centers. As previously discussed, they form due to the PEG being trapped in interfibrillar regions during PLA spherulite growth. Observing the cross-section of the film in the same image further confirms that PEG was homogeneously distributed throughout the entire thickness. Additionally, the presence of stratified structures on the film upper edge closely resembles the morphology observed in SEM images

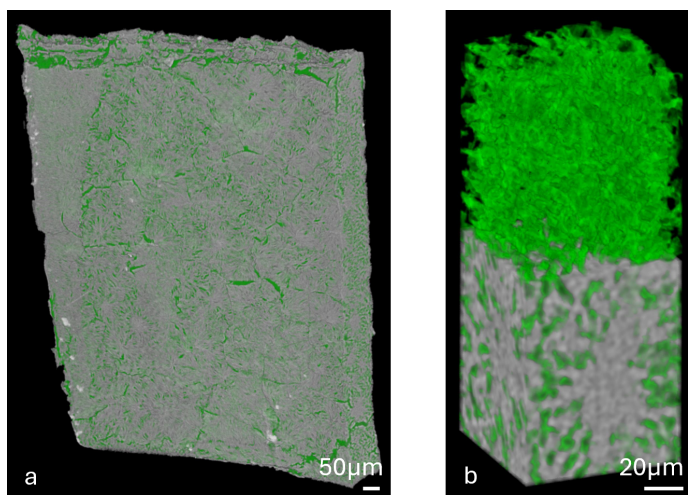


Fig. 3.8 Micro-CT scan of a PLA/PEG100K 70/30 film, with pores highlighted in green and PLA in gray. (a) Full view of the film structure. (b) A magnified section of the bulk, where the solid PLA has been digitally removed in the upper region to enhance the visualization of the porous network.

(Figure 3.4 (b)). Overall, both the surface and cross-sectional views in Figure 3.8(a) are consistent with previous SEM observations. However, some bright white spots appear in the image, which likely correspond to impurities within the material.

Figure 3.8 (b) provides a magnified view of the film bulk to visualize its internal structure. This figure is divided into two sections: in the lower half, PLA is displayed in gray, while pores are highlighted in green, preserving the same representation as in Figure 3.8 (a). This region exhibits a homogeneous porosity distribution, similar to that observed on the film surface. In the upper half, the PLA matrix has been digitally removed, revealing the internal porosity of the material. The interconnected nature of the pores is clearly visible, demonstrating the formation of a continuous porous network. Although precise evaluation from this image alone is challenging, the porosity distribution and shape appear highly similar to that observed in SEM images of Figure 3.5. Micro-CT analysis also allows for the quantification of total porosity, which is measured at approximately 28% in volume. This value aligns well with the initial PEG content in the material. However, it remains somewhat surprising given that NMR and

XRD results indicate that around 10% of PEG remains within the material after extraction. Since the pore size, on the order of microns, is close to the resolution limit of the Micro-CT scanner, porosity may be overestimated due to an inaccurate assessment of pore interconnectivity, which could be artificially amplified by the imaging resolution. In addition, part of the discrepancy may arise from the comparison between mass fraction values obtained by NMR and XRD and the volume fraction derived from Micro-CT measurements. Differences in density between PLA and PEG mean that a given mass fraction does not correspond to the same volume fraction; thus, interpreting porosity based on volume while residual PEG is quantified by mass can lead to apparent inconsistencies.

3.2.5 Dual porosity in 3D-printed objects

After characterizing microporosity in thin films, it is necessary to evaluate whether similar porosity can be achieved after 3D printing the material. To enable this, PLA/PEG filaments were produced in a two-step extrusion process.

In the first step, a preliminary mixing was performed using a twin-screw extruder, where PLA and PEG were co-extruded into continuous strands that were subsequently cut into pellets. Since PLA is supplied in pellet form and PEG as a powder, this initial extrusion step is essential to ensure a sufficiently homogeneous PLA/PEG blend.

In the second step, these PLA/PEG pellets were extruded again using a single-screw extruder specifically designed for filament production. The filament diameter was continuously monitored during extrusion, with a feedback loop maintaining it within a $\pm 50 \mu\text{m}$ range. The resulting filament exhibited a sufficiently uniform diameter and homogeneous composition to allow for high-quality 3D printing. This method is described in detail in Chapter 1.

While PEG molar mass had a limited impact on porosity formation in PLA/PEG films, it played a critical role in the feasibility of 3D printing. The viscosity variations induced by different PEG molar masses significantly affected both filament quality and printability. For PLA/PEG3K 70/30 samples, the blend was too fluid, preventing the formation of a printable filament. Conversely, for PLA/PEG1M 70/30, a filament could be produced; however, the high viscosity of PEG resulted in compositional heterogeneity, leading to inconsistent filament quality and insufficient filament length for

successful printing. As a result, only the PLA/PEG100K 70/30 composition was suitable for 3D printing, as it provided the optimal balance between viscosity, homogeneity, and filament integrity.

Therefore, in order to assess the porosity of 3D-printed materials, various samples were produced using a PLA/PEG100K 70/30 filament. Initially, solid cubes with a side length of 1 cm (without macroporosity) were printed using default printing parameters. The build platform temperature was set to 30°C, while the extrusion temperature was maintained at 200°C. Once printed, PEG was extracted from the cubes following the previously described procedure. The samples were then sectioned, and the cross-sections were examined using SEM. The resulting images are presented in Figure 3.9.

Figure 3.9 (a) shows the intersected filaments forming the structure. The lower left corner of the image exhibits a clean cut, whereas the upper right edge appears torn. This difference arises from the cutting process: at a certain point, the sample fractured naturally, providing a more representative cross-section of the material. In contrast, direct cutting often results in surface smoothing due to the interaction with the blade. The fractured region better reveals the internal morphology, showing both the filament arrangement and the spherulitic structures within the filaments.

A closer view in Figure 3.9 (b) provides further details of the spherulites in the cross-section. Although their morphology resembles that observed in films crystallized at 110°C (see Figure 3.3 (a)), they are significantly smaller. This size reduction is attributed to the absence of controlled post-melting crystallization, as opposed to the forced crystallization in films. Instead, the rapid cooling inherent to the 3D printing process increased nucleation density, leading to smaller spherulites.

Despite the fast and uncontrolled cooling during 3D printing, an important observation is that PEG still acted as a plasticizer, allowing PLA to crystallize. A higher magnification of the spherulitic surface reveals porosity resulting from PEG extraction. This confirms that microporosity can still be achieved after 3D printing. The cooling rate, though rapid, remains slow enough to enable phase separation between PLA and PEG, allowing PEG extraction and the formation of microporosity.

Now that it has been demonstrated that 3D-printed objects can be made microporous, the next step is to combine phase separation and 3D printing to develop materials with hierarchical porosity. For this purpose, a 3D macroporous gyroid structure was designed, as shown in Figure 3.10, from

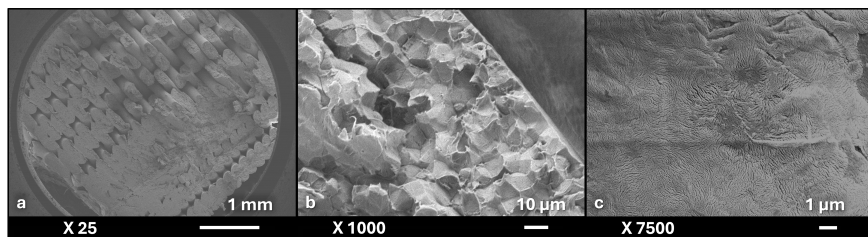


Fig. 3.9 SEM images of the bulk of a 3D-printed PLA/PEG100K 70/30 object after PEG extraction, highlighting the microporosity obtained after the shaping process. The images are presented at increasing magnification: printed filaments (a), spherulitic structures inside the filaments (b), and microporosity on the spherulite surfaces (c).

the top (a) and from the side (b). This model was then 3D-printed, followed by PEG extraction under the same conditions as previously described.

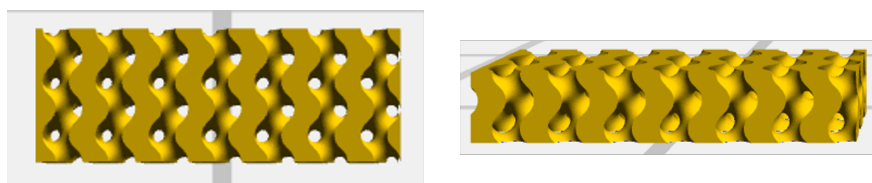


Fig. 3.10 3D model of a gyroid-based macroporous structure. Top view (left) and side view (right).

After printing and extraction, the sample was sectioned, and its cross-section was analyzed via SEM. The resulting images are presented in Figure 3.11. In Figure 3.11 (a), the macroporosity induced by 3D printing is clearly visible. A closer examination of the cross-section surface in Figure 3.11 (b) reveals PLA spherulites, within which relatively large pores can be observed. These elongated black regions resemble "cracks" within the material and correspond to PEG-rich regions that, once extracted, leave behind larger pores. This morphology was previously observed in thin films, particularly in Figures 3.2 (b) and (c), as well as in Figure 3.4 (a).

Further magnification in Figure 3.11 (c) reveals the fine porosity characteristic of PEG extraction following phase separation with PLA. It is worth noting that the slightly larger porosity resulting from PEG accumulation in specific regions (Figure 3.11 (b)) is relatively difficult to control. However, macroporosity is directly dictated by the 3D model and is therefore highly

tunable. Additionally, the fine microporosity appears consistent between films and 3D-printed objects, suggesting that it can be controlled and homogeneously distributed throughout the material. The creation of hierarchical porosity is therefore achievable and can be efficiently realized through the 3D printing of PLA/PEG blends.

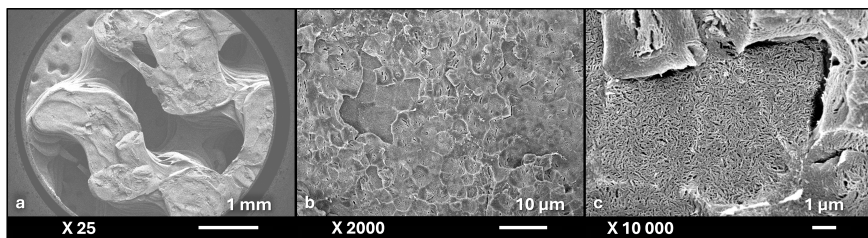


Fig. 3.11 SEM images of a sliced 3D-printed macroporous PLA/PEG100K 70/30 object after PEG extraction, illustrating its hierarchical porosity. The images show the macroporous architecture (a), spherulites at the slice surface (b), and microporosity within the bulk (c).

3.2.6 Conclusions

The analysis of porosity in PLA/PEG blends demonstrated that microporosity is consistently achieved across different sample types, including thin films and 3D-printed objects. In solvent-extracted films, SEM imaging revealed a well-distributed microporous network, with pores forming predominantly in interfibrillar and interspherulitic regions due to PEG phase separation during PLA crystallization. Micro-CT imaging further confirmed this distribution in three dimensions, showing a homogeneous porosity throughout the material thickness. Although porosity was estimated at approximately 28%, the resolution limits of Micro-CT may have led to a slight overestimation due to the artificial enhancement of pore interconnectivity.

The successful integration of porosity into 3D-printed objects indicates that hierarchical porous structures can be created by combining phase separation and additive manufacturing. Despite the rapid and uncontrolled cooling during 3D printing, the plasticizing effect of PEG allowed sufficient PLA crystallization, leading to microporosity comparable to that observed in films. Moreover, the use of controlled 3D-printed geometries enabled the introduction of macroporosity, which remains highly tunable, while microporosity maintained its consistent distribution within the material.

However, the feasibility of producing printable filaments strongly depended on PEG molar mass, with low molar mass PEG leading to excessive fluidity and high molar mass PEG causing inhomogeneities, leaving only intermediate molar mass PEG suitable for printing.

Additionally, the molar mass of PEG influenced both its extractability and the resulting porosity. Higher molar mass PEG exhibited greater entanglement with PLA chains, making its removal slightly less efficient. However, in all cases, a residual PEG content of 7–10% was observed, independent of sample thickness, suggesting that the extraction process was effective and that the remaining PEG was primarily trapped within the interlamellar amorphous PLA phase.

Overall, these results confirm that hierarchical porosity can be achieved in PLA/PEG blends through phase separation, with both microporosity and macroporosity being tunable depending on processing conditions and material composition.

4

Mechanical properties of porous PLA/PEG materials

To conclude this research, it is essential to evaluate the mechanical performance of PLA/PEG blends before and after PEG extraction. While porosity significantly alters the structural properties of these materials, their mechanical behavior remains a key criterion in determining potential applications. To characterize these properties, tensile tests were conducted on dogbone-shaped specimens following the ISO 527-2-5A standard. A broad range of parameters was investigated, including the effects of 3D printing, macro- and microporosity, their combination in hierarchical porosity, as well as the effect of thermal annealing to promote crystallization after 3D printing.

4.1 Description and categorization of the samples

To investigate the influence of those parameters a set of samples was prepared using different fabrication and post-processing techniques. These samples can be categorized into three main groups: injection-molded PLA references, 3D-printed commercial PLA samples and PLA/PEG100K 70/30 blends with varying porosity and thermal treatments.

The injection-molded (IM) PLA samples serve as baseline references for evaluating the intrinsic properties of PLA in the absence of structural defects. These samples are considered defect-free and thus allow for a clear assessment of the impact of 3D printing-induced defects, such as inter-layer porosity or adhesion issues, on the mechanical performance of the material, as discussed in the section 4.2 about additive manufacturing in the Context of the Research. The sample "IM HP2500" is fabricated from PLA grade HP2500, a formulation specifically engineered by NatureWorks to promote crystallization. In contrast, the "IM cPLA" sample is produced using a commercial PLA filament supplied by default with the 3D printer at purchase. This latter material is intended for additive manufacturing and is thus optimized for printability rather than crystallization behavior. The comparison between these two injection-molded formulations provides a reference point for understanding how material composition and intended processing routes influence mechanical properties independently of print-induced structural artifacts.

The 3D-printed cPLA samples, fabricated using commercial PLA filament, serve as reference materials for evaluating the structural and mechanical characteristics of printed objects, both with and without designed macroporosity. These samples establish a baseline for assessing the influence of additive manufacturing independently of any compositional modifications. They are subsequently compared with PLA/PEG blend samples to isolate and highlight the specific effects of polymer blending, particularly in relation to phase separation and the induced porosity and resulting mechanical performance. The standard "cPLA" sample represents 3D-printed commercial PLA, whereas the "cPLA P16" and "cPLA P20" samples include macroporosity of different sizes to assess the influence of macroporosity on the material mechanical properties. P16 and P20 corresponds to a cell size of 16 and 20 mm respectively. To better highlight the differences between P16 and P20, Figure 4.1 presents top-view images (left) and side-view images (right) of P16 (top) and P20 (bottom), illustrating their distinct macroporous architectures. These samples were designed with a total porosity of 50%, but the unit cell size varies. A smaller unit cell (P16) results in a higher number of repeating structures within a given volume, requiring thinner walls to maintain the overall porosity. Conversely, a larger unit cell (P20) leads to fewer repeating structures but with thicker walls to compensate and preserve the 50% porosity. In the dogbones, the macroporosity is incorporated in the middle of the gage, as represented in the bottom right of the Figure 4.1, compared to the standard dogbones in the bottom left.

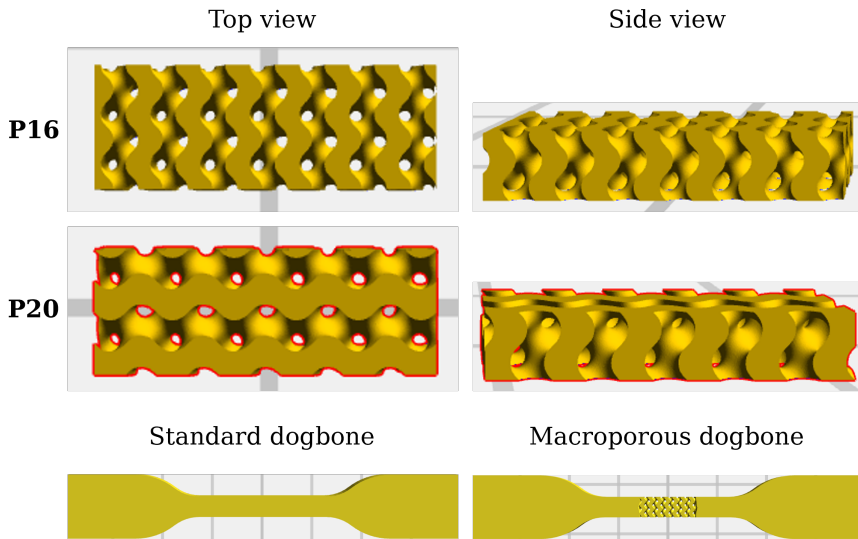


Fig. 4.1 Comparison of macroporosity created with cell size of 16mm (P16) and 20mm (P20). Top-view (left) and side-view (right) images of P16 (top) and P20 (bottom). Both samples were designed with a total porosity of 50%. Standard and macroporous dogbones are presented in the lower left and lower right sections, respectively.

The PLA/PEG blends investigate the effect of PEG as a plasticizer and the role of phase separation in generating hierarchical porosity. The "Blend" sample represents the initial state of the polymer mixture, PLA/PEG100K 70/30, highlighting the plasticizing effect of PEG. The "Blend ext." sample results from PEG extraction, leaving behind a microporous PLA structure, which allows for the study of microporosity effects. Note that the PLA used in the blends is always the PLA HP2500.

Additional treatments were applied to some of the blends to further investigate their behavior. As previously discussed, crystallizing the blend from the melt is not feasible with our equipment when using 3D printing, unlike in blend films. To assess the effect of annealing after solidification, the "Blend ann." sample was annealed at 110°C for 4 hours, providing insight into the impact of thermal treatment on crystallization and phase separation. The "Blend ann. ext." sample underwent both annealing and PEG extraction, enabling the simultaneous evaluation of crystallinity changes and microporosity formation.

Finally, non-annealed PLA/PEG blends with macroporosity ("Blend P16" and "Blend P20") were prepared to study the interaction between macroporosity and PEG plasticization. Their counterparts, "Blend P16 ext." and "Blend P20 ext.", underwent PEG extraction, resulting in materials with both macro- and microporosity, enabling a comprehensive analysis of hierarchical porosity effects.

The names and brief descriptions of all the samples analyzed are summarized in Table 4.1, in order to clarify and facilitate the comparison of the specific objectives associated with each sample.

Table 4.1 Description of the studied samples used for traction tests.

Sample Name	Description
IM HP2500	PLA HP2500 processed by injection molding → Used as defect-free reference
IM cPLA	Commercial PLA processed by injection molding → Used as comparison with PLA HP2500
cPLA	Commercial PLA printed in 3D → To highlight the effect of 3D printing compared to IM samples
cPLA P16	Commercial PLA printed in 3D with a macroporosity of 16 → To highlight the effect of macroporosity P16
cPLA P20	Commercial PLA printed in 3D with a macroporosity of 20 → To highlight the effect of macroporosity P20
Blend	PLA/PEG100K 70/30 blend (all the following blends have the same composition) → Used as reference for all other 3D printed blends
Blend ext.	PLA/PEG blend after PEG extraction → To highlight the effect of PEG extraction in the blend
Blend ann.	PLA/PEG blend annealed at 110°C for 4h after printing → To highlight the effect of annealing on 3D printed blends
Blend ann. ext.	PLA/PEG blend annealed at 110°C for 4h after printing and PEG extraction → To highlight the combined effect of annealing and PEG extraction
Blend P20	PLA/PEG blend with a macroporosity of 20 → To highlight the effect of macroporosity P20 on 3D printed blends
Blend P20 ext.	PLA/PEG blend with a macroporosity of 20 after PEG extraction → To highlight the combined effect of macroporosity and PEG extraction
Blend P16	PLA/PEG blend with a macroporosity of 16 → To highlight the effect of macroporosity P16 on 3D printed blends
Blend P16 ext.	PLA/PEG blend with a macroporosity of 16 after PEG extraction → To highlight the combined effect of macroporosity and PEG extraction

Table 4.2 Summary of mechanical properties extracted from traction test and crystallinity measured by DSC for all samples with E, the Young modulus; ϵ_b , the elongation at break; σ_m , the ultimate tensile strength; T, the toughness; and X_c , the crystallinity.

	E [GPa]	ϵ_b [%]	σ_m [MPa]	T [MJ/m ³]	X_c [%]
IM HP2500	2.09	5.19	79.35	2.49	28
IM cPLA	2.11	4.89	66.89	2.08	10
cPLA	1.49	5.01	40.82	1.40	6
cPLA P16	1.00	2.48	11.80	0.25	-
cPLA P20	0.91	2.77	10.02	0.46	-
Blend	0.40	103.00	11.40	12.72	60
Blend ext.	0.66	55.21	17.19	8.29	47
Blend ann.	0.63	10.44	16.55	1.41	77
Blend ann. ext.	0.89	4.59	18.61	0.62	76
Blend P20	0.21	12.82	3.69	0.59	56
Blend P20 ext.	0.38	4.87	5.27	0.44	44
Blend P16	0.31	7.48	5.33	0.46	57
Blend P16 ext.	0.43	3.88	5.90	0.27	45

4.2 Mechanical performance of porous blends

4.2.1 Reference samples

To support the interpretation of the tensile results, four reference samples were selected to serve as mechanical benchmarks throughout the analysis: (I) IM HP2500, characterizing the intrinsic properties of semicrystalline PLA HP2500 in the absence of structural defects, (II) IM cPLA, providing a formulation-based comparison with the PLA used in printed samples and blends, (III) cPLA, representative of the mechanical response of standard 3D-printed PLA objects, and (IV) cPLA P20, incorporating designed macroporosity as a structural reference. These four specimens form a comparative framework to assess the influence of PEG incorporation, thermal treatment and hierarchical porosity on the mechanical performance of the different systems.

Based on the tensile test results, mechanical properties were analyzed. For each sample, the Young's modulus (E), ultimate tensile strength (σ_m), elongation at break (ϵ_b) and area under the stress-strain curve (T), which provides an approximation of the material's toughness, were determined. All these values are gathered in the Table 4.2. The results will be discussed with the aim of highlighting the targeted properties, specifically the effects of polymer blending and thermal annealing, as well as the respective contributions of microporosity, macroporosity, and hierarchical porosity.

To complement the individual analysis of the different effects, a final graph compiling all the samples is presented at the end of this chapter. This overview plot displays the primary mechanical characteristics, specifically Young's modulus and elongation at break, to provide a comparative visualization of the combined influence of polymer blending, thermal annealing, micro- and macroporosity, and their hierarchical organization. Additionally, to support the interpretation of these results, crystallinity was measured via DSC after tensile testing. Crystallinity was evaluated at two different locations: near the fracture surface and in a region further from the break where the sample experienced minimal deformation. As the values were highly similar, only the crystallinity measured near the fracture is reported.

Figure 4.2 presents the mechanical properties of the four reference samples, including Young's modulus (E), maximum stress (σ_m), elongation at break (ϵ_b), toughness (T) and crystallinity (X_c). All mechanical parameters are derived from tensile tests and the results are displayed on logarithmic axes to accommodate the broad range of values across the dataset. Crystallinity was measured by DSC after tensile testing.

The first comparison examines the difference between the PLA used in the blend (IM HP2500) and commercial PLA (IM cPLA). Both materials exhibit similar Young's modulus values, although the ultimate tensile strength of IM cPLA is slightly lower. Both polymers demonstrate high rigidity and brittleness, as indicated by their low elongation at break and limited energy absorption before failure. The toughness, approximated by the area under the stress-strain curve, confirms their brittle nature, as these materials undergo minimal plastic deformation prior to rupture. However, despite these mechanical similarities, the crystallinity of PLA HP2500 is nearly three times higher than that of commercial PLA. Crystallinity is generally associated with increased stiffness and strength, as crystalline domains restrict chain mobility. However, this effect is not clearly reflected

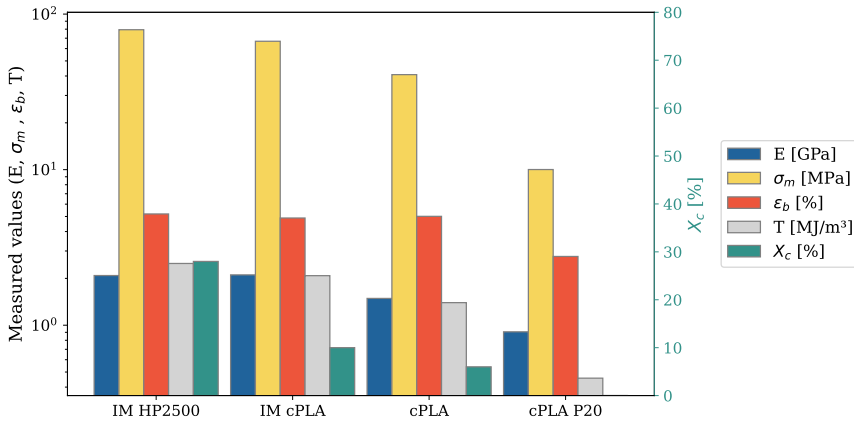


Fig. 4.2 Mechanical properties and crystallinity of reference samples (IM HP2500, IM cPLA, cPLA, cPLA P20). Young's modulus (E), maximum stress (σ_m), elongation at break (ϵ_b) and area under stress-strain the curve (T) were determined from tensile tests. Crystallinity (X_c) was determined from DSC measurement carried out on the samples after the mechanical testing. For the cPLA P20 sample, crystallinity was not measured.

in the present mechanical data. Indeed, in the work of Harris and Lee [134], the authors demonstrated that crystallinity enhances the flexural modulus of injection-molded PLA. Although the flexural modulus and Young's modulus generally follow the same trend, especially when parameters such as crystallinity are modified, the magnitude of their variation may differ due to the distinct loading modes they represent. Therefore, other parameters may be involved, including the size of the spherulites that can be controlled by nucleating agents and affects toughness, but they will not be further investigated.

Comparing IM cPLA and cPLA provides insight into the effects of 3D printing on mechanical properties. In general, 3D printing results in an approximate 30% reduction in mechanical performance compared to injection molding. This decline is attributed to multiple factors. First, 3D printing is an additive manufacturing process in which molten polymer layers are sequentially deposited. Depending on printer quality and processing parameters, misalignment between layers can introduce structural imperfections. If the deposited filaments are not perfectly fused, unintended heterogeneously distributed porosity forms in the material, acting

as stress concentrators that reduce mechanical strength. Second, interlayer adhesion plays an important role in mechanical integrity. The degree of interlayer diffusion varies depending on factors such as print temperature, layer thickness, and printing speed, all of which influence the mechanical performance of the printed object. Beyond local defects, the deposition process itself introduces directional dependence in mechanical performance. Von Windeheim and coworkers [103] demonstrated that crystallinity has a moderate impact on the mechanical properties of 3D-printed objects, as the welds between printed filaments create weak points in the material, and no co-crystallization occurs between layers to strengthen the interface. The same conclusions were obtained by Luzanin et al. [104], who showed that crystallinity does not impact significantly the tensile strength.

The final reference sample, cPLA P20, corresponds to the dogbone specimen incorporating macroporosity, as shown in Figure 4.1. As expected, a decrease in mechanical properties is observed due to the 50% porosity in the cross-section compared to solid dogbones. However, it is notable that while Young's modulus decreases by only 30%, ultimate tensile strength undergoes a much more substantial reduction of approximately 70%. This discrepancy suggests that the failure mechanism is highly influenced by stress concentration effects around macropores. In porous materials, localized stress amplification at the edges of pores promotes premature failure, affecting ultimate tensile strength. In contrast, Young's modulus, which primarily reflects the elastic response of the material, is less affected because it is determined by the stiffness of the remaining solid structure rather than by fracture initiation. This highlights the significant impact of macroporosity on the mechanical integrity of 3D-printed structures.

Having established the mechanical baselines associated with material composition, fabrication method, and macroporosity, the next sections focus on the additional influence of PEG addition and its plasticization effect, thermal annealing, microporosity and hierarchical porosity. The reference sample corresponding to each structural or compositional modification is positioned on the far left of each graph for clarity.

4.2.2 Effect of blending and thermal annealing

The first aspect analyzed is the effect of blending, particularly the incorporation of PEG into PLA, as shown in Figure 4.3. Comparing IM HP2500 and Blend samples reveals a significant reduction in stiffness—Young’s modulus decreases from 2.09 GPa to 0.4 GPa—accompanied by a substantial increase in ductility, with elongation at break rising from 5% to 103%. This confirms the strong plasticizing effect of PEG, which lowers the glass transition temperature of amorphous PLA-rich regions below room temperature. As a result, chain mobility is enhanced, stiffness decreases, and the material absorbs more energy before fracture, leading to a marked increase in toughness.

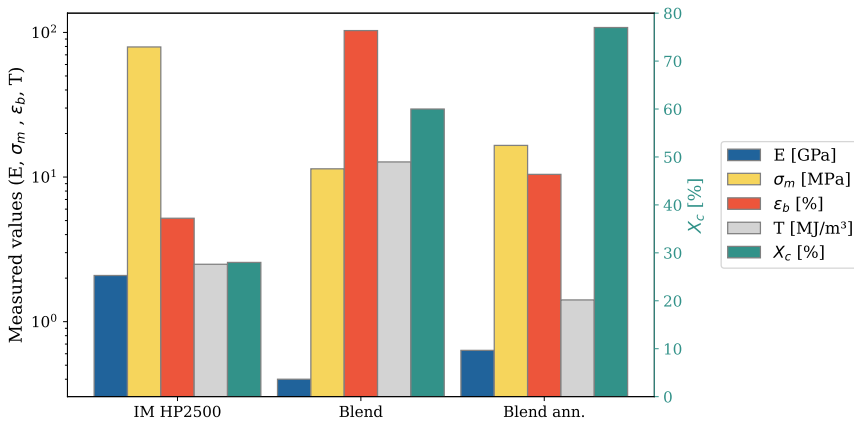


Fig. 4.3 Mechanical properties and crystallinity of PLA/PEG100K 70/30 blends samples (Blend, Blend ann.) compared to IM HP2500 used as reference. Young’s modulus (E), maximum stress (σ_m), elongation at break (ϵ_b) and area under stress-strain the curve (T) were determined from tensile tests. Crystallinity (X_c) was determined from DSC measurement carried out on the samples after the mechanical testing.

In addition to modifying the mechanical response, PEG also promotes PLA crystallization, as indicated by the increase in crystallinity from 28% to 60%. Although this dual role may seem contradictory, it is explained by the heterogeneous nature of the blend: PEG enhances crystallization through T_g depression, while simultaneously remaining in the amorphous phase to maintain chain mobility. The resulting material exhibits high crystallinity

yet remains flexible and deformable. This align well with the work of Mohapatra et al. [81], who demonstrated a similar plasticizing effect in PLA/PEG 70/30 injection-molded samples. A similar trend was also observed by Kumar et al. [120] with a PEG content of 5% in injection molding. However, at such a low PEG concentration, this effect did not significantly influence the mechanical properties of 3D-printed samples.

The effect of annealing, shown by the comparison between Blend and Blend ann., further modifies these properties, leading to an increase in Young's modulus and ultimate tensile strength. However, this gain in stiffness is accompanied by a sharp reduction in elongation at break. A similar trend has been observed in pure PLA, where annealing increases the Young's modulus; however, the elongation at break is slightly reduced [59]. While an increase in crystallinity is expected to enhance stiffness, the observed decrease in ductility appears disproportionately high given the relatively moderate increase in crystallinity, this indicates a significant loss of the plasticizing effect of PEG. Indeed, during annealing at 90°C, PEG transitions into the molten state and partially migrates out of the material, as evidenced by the presence of liquid PEG observed on the glass plate after the annealing step. This phenomenon is facilitated by liquid-solid phase separation, as PLA crystallization further excludes PEG from its spherulitic structure, effectively reducing the PEG content in the bulk material. Consequently, the plasticizing effect of PEG is reduced due to its partial loss, leading to a more brittle mechanical response.

Another explanation is that, during annealing, PLA spherulites grow and expel PEG into interspherulitic regions. This mechanism does not preclude the first one; both phenomena may occur simultaneously and contribute to the observed behavior. This redistribution lead to large PEG-rich zones, creating mechanically weak interfaces. Such phase-separated PEG domains act as stress concentrators or weakness in interspherulitic regions, as it prevents a good cohesion between the PLA spherulites, reducing the material's overall toughness. This behavior is similar to what was observed in PLA/PEG 50/50 blends discussed in the previous chapter, where excessive PEG accumulation in interspherulitic regions resulted in increased brittleness. In both cases, the key factor appears to be the localization of PEG: when well-dispersed, it effectively plasticizes the material, but when segregated, it introduces structural weaknesses that compromise mechanical integrity.

A direct comparison between the annealed blend (Blend ann.) and the IM HP2500 reference sample reveals a surprising observation: despite the crystallinity being more than twice as high in the Blend ann. sample, its Young's modulus is significantly lower. This indicates that crystallinity alone cannot account for the observed reduction in stiffness. Instead, the fabrication process, in this case, 3D printing, also plays a crucial role in defining the mechanical behavior. As previously discussed in the section on reference samples, 3D printing introduces structural heterogeneities and interlayer interfaces that limit mechanical performance compared to injection molding.

Additionally, while the nominal PEG content in the blend is 30%, a portion of it migrated out of the sample during annealing, as evidenced by the presence of PEG residue on the substrate. Consequently, the actual PEG content is lower than expected, which leads to an overestimation of PLA crystallinity in the DSC analysis, since part of the amorphous phase has been removed. Despite this loss, a fraction of PEG remains within the material. Although its precise concentration is unknown, its plasticizing effect is still evident: the sample shows reduced stiffness and increased elongation at break compared to neat PLA. This further confirms the dual influence of both PEG content and 3D printing-induced morphology on the mechanical response of the material.

4.2.3 Effect of microporosity

Following the analysis of PEG blending, the effect of microporosity on mechanical behavior is examined, as shown in Figure 4.4. This effect is investigated through the 3D-printed PLA/PEG samples after PEG extraction. The observed trends remain similar to those of the non-extracted samples, although the plasticizing influence of PEG is significantly reduced. This result is expected, as a significant portion of PEG has been removed from the material. The removal of PEG induces the opposite effect of its plasticization: an increase in Young's modulus and a decrease in elongation at break. This "reversible" behavior, softening upon PEG addition and stiffening upon its removal, has not been previously reported in the literature.

A particularly relevant observation is that the impact of microporosity appears relatively limited compared to that of blending itself. Despite the presence of microporosity, the material retains a relatively high elongation

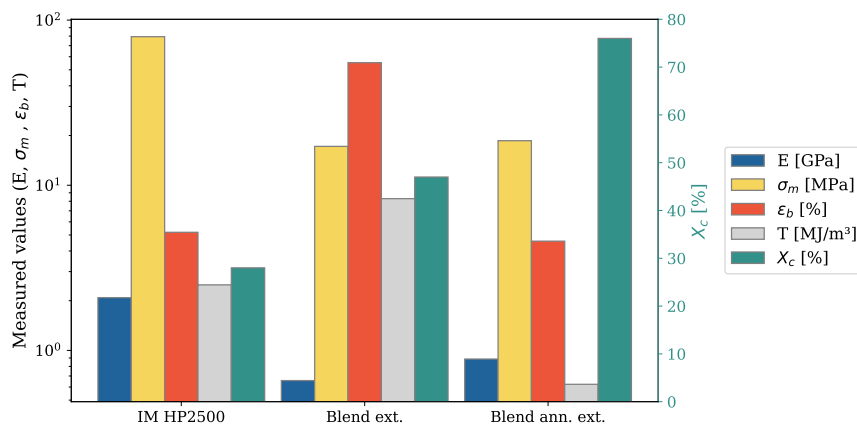


Fig. 4.4 Mechanical properties and crystallinity of microporous samples (Blend ext. and Blend ann. ext.) compared to IM HP2500 used as reference. Young's modulus (E), maximum stress (σ_m), elongation at break (ϵ_b) and area under stress-strain the curve (T) were determined from tensile tests. Crystallinity (X_c) was determined from DSC measurement carried out on the samples after the mechanical testing.

at break and a low Young's modulus, indicating that it remains highly deformable. For instance, after PEG extraction, the Young's modulus increases from 0.40 GPa (Blend) to 0.66 GPa (Blend ext.), while elongation at break decreases from 103% to 55%. Although this stiffening effect is significant, the material remains much more flexible than neat PLA (IM HP2500, $E = 2.09$ GPa, $\epsilon_b = 5\%$).

These results suggest that the mechanical behavior is still largely governed by the residual polymer matrix rather than by the voids generated by PEG extraction. This could be attributed to the fine, homogeneous distribution of micropores, which limits the formation of critical stress concentrators and allows the material to maintain its ductility.

Additionally, annealing once again increases crystallinity while drastically reducing elongation at break. The underlying mechanisms are similar to those described for the Blend ann. sample. The crystallization of PLA upon annealing leads to a stiffening of the material, while the reduction in chain mobility causes a sharp loss of ductility. This is well illustrated by the transition from $E = 0.66$ GPa, $\epsilon_b = 55\%$ (Blend ext.) to $E = 0.89$ GPa, $\epsilon_b = 5\%$ (Blend ann. ext.), confirming that the annealing-induced increase in crystallinity, from 47% to 76%, leads to a highly brittle structure. These

results clearly show that crystallinity-driven embrittlement dominates over any residual plasticizing effect of PEG.

In summary, microporosity has a less pronounced influence on mechanical performance than blending itself. While PEG removal increases stiffness and reduces elongation at break, the mechanical response remains largely governed by the initial phase-separated morphology of the PLA/PEG system. Additionally, the combination of PEG extraction and annealing results in a highly crystalline and brittle structure, in stark contrast to the flexible and tough nature of the non-annealed blend.

4.2.4 Effect of macroporous structures

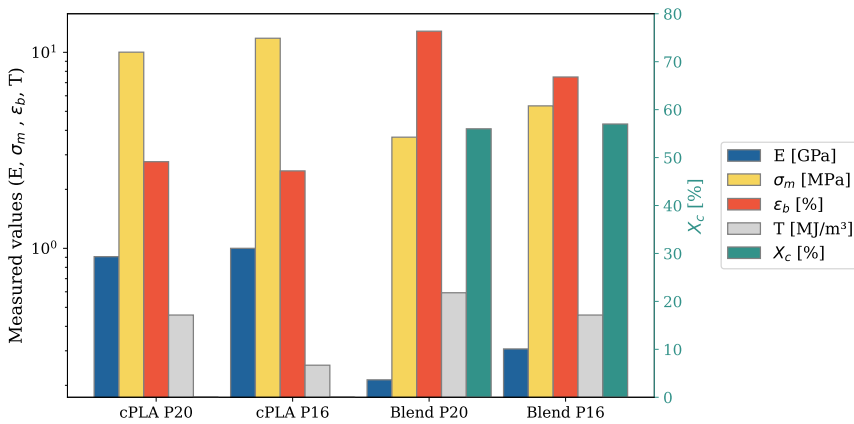


Fig. 4.5 Mechanical properties and crystallinity of macroporous samples (cPLA P16, Blend P20 and Blend P16) compared to cPLA P20 used as reference. Young's modulus (E), maximum stress (σ_m), elongation at break (ϵ_b) and area under stress-strain the curve (T) were determined from tensile tests. Crystallinity (X_c) was determined from DSC measurement carried out on the samples after the mechanical testing.

As previously described in Figure 4.2, macroporosity has a significant impact on the mechanical properties of the material, generally leading to a reduction in strength and stiffness due to stress concentration and reduced load-bearing cross-sections. However, several parameters can be adjusted to tailor this macroporosity and influence the resulting mechanical behavior.

One of the first aspects to consider is the effect of blending. Even in

the presence of macroporosity, the plasticizing effect of PEG significantly modulates the mechanical response of the system. This is evident when comparing the cPLA P20 and cPLA P16 samples with their Blend P20 and Blend P16 counterparts, as shown in Figure 4.5. In parallel, the design of macroporosity itself offers another avenue to tailor the mechanical behavior, as evidenced by the differences between the P20 and the P16 samples.

Incorporating PEG into the macroporous structures substantially reduces stiffness and strength while enhancing ductility. This trend is consistent across both P16 and P20 geometries and clearly illustrates the dominant plasticizing effect of PEG, even in the presence of large-scale porosity. Compared to their cPLA counterparts, the PLA/PEG blends exhibit lower Young's modulus and ultimate tensile strength, but higher elongation at break. Although crystallinity was not measured for the cPLA P16 and P20 samples, it is noteworthy that within the PLA/PEG blends, both P16 and P20 exhibit very similar crystallinity values, despite showing markedly different mechanical responses. This suggests that crystallinity alone does not account for the observed differences. The fact that the relative trends between P16 and P20 are similar for both the cPLA and the blends strongly supports the conclusion that the macroporous architecture — and specifically the unit cell size — is a key factor governing the mechanical behavior in these systems.

In both the cPLA and their blends counterparts, samples with smaller cell sizes (P16) systematically exhibit higher Young's modulus and ultimate tensile strength compared to those with larger cells (P20). This mechanical enhancement can be attributed to differences in cell topology and mass distribution rather than to variations in overall density. The denser arrangement of thinner walls in P16 creates a more interconnected network, which constrains local deformation and facilitates stress transfer across the structure. This results in a more homogeneous load distribution and greater overall stiffness. In contrast, the P20 structure, characterized by fewer but thicker walls, allows for more localized deformation and stress concentration, thereby reducing the apparent stiffness and strength.

This behavior aligns with the predictions of the Gibson-Ashby model [135, 136], which describes the mechanical properties of cellular materials as a function of their relative density and structural arrangement. According to Gibson and Ashby, the Young's modulus E_p of a cellular material is related to the Young's modulus of the solid material E_s as:

$$E_p = CE_s \left(\frac{\rho_p}{\rho_s} \right)^n$$

where ρ_p and ρ_s are the densities of the cellular and solid material, respectively, C is a constant dependent on the cell geometry, and n typically ranges from 1.5 to 2 for open-cell structured porous materials. Furthermore, for periodic cellular structures such as those in this study, the ratio of ρ_p/ρ_s also depends on the ratio of wall thickness (t) to cell size (l) [135]:

$$\left(\frac{\rho_p}{\rho_s} \right) \propto \left(\frac{t}{l} \right)$$

At constant porosity, this implies a fixed t/l ratio. Under such conditions, the classical scaling law would predict identical stiffness for structures sharing the same relative density. However, Gibson and Ashby also emphasize that, for densities with $\rho_p/\rho_s > 0.2$, the mechanical response of cellular solids becomes increasingly sensitive to architectural parameters beyond relative density alone, including anisotropy and cell connectivity.

The present comparison between P16 and P20 structures, both designed at 50% porosity, illustrates precisely this point. Although the t/l ratio remains constant, the P16 architecture, with smaller cell size l , exhibits a denser network of struts and junctions per unit volume. This increased structural connectivity enhances mechanical constraint and promotes a more uniform stress distribution, leading to a higher effective stiffness. Conversely, the coarser structure of P20, with fewer load paths and less constraint, is more compliant. Therefore, even though the global porosity is unchanged, cell topology plays a decisive role in governing the mechanical performance.

Beyond its impact on stiffness, cell topology also plays an important role in failure behavior. Tensile testing of Blend P16 and Blend P20 samples revealed that fracture does not occur as a single abrupt event but rather progresses in a stepwise manner, with failure occurring incrementally. This behavior is characteristic of macroporous PLA/PEG samples, where crack propagation is intermittent, in contrast to macroporous cPLA samples, which undergo a sharp and continuous fracture. This difference arises from the structural homogeneity of pure PLA compared to the heterogeneous nature of PLA/PEG blends. In Blend P20 and Blend P16 samples, the presence of PEG domains creates variations in local mechanical resistance.

Additionally, PEG acts as a plasticizer in the PLA matrix, reducing its stiffness and increasing its ductility. This plastification effect influences crack propagation by delaying the localization of stress, leading to a more progressive failure mechanism rather than an abrupt fracture. In macroporous PLA/PEG structures, where the cell walls are already thin, the increased flexibility due to PEG further enhances this stepwise rupture, as individual cell walls can deform before failing. By contrast, pure PLA, being a single-phase material with no plastifying agent, does not exhibit this behavior. Once a crack is initiated, it propagates unimpeded through the structure, resulting in a rapid failure. In non-macroporous PLA/PEG samples, Blend and Blend ext., whether PEG is present or has been extracted, crack propagation remains continuous, as the absence of macroporosity eliminates structural interruptions that could induce stepwise failure.

These results demonstrate that mechanical properties can be tailored according to the specific application requirements by selecting the appropriate macroporosity design and cell size.

4.2.5 Effect of hierarchical porosity

Finally, the effect of hierarchical porosity, combining both macroporosity and microporosity, is analyzed in Figure 4.6. The results are normalized against the macroporous commercial PLA sample (cPLA P20) to facilitate comparison. As previously discussed, the effect of blending, even after PEG extraction, continues to play an important role due to the residual plasticizing effect of PEG. A decrease in Young's modulus and an increase in elongation at break are again observed, consistent with the trends reported in previous sections.

Specifically, comparing Blend P20 ext. ($E = 0.38$ GPa, $\epsilon_b = 5\%$) and Blend P16 ext. ($E = 0.43$ GPa, $\epsilon_b = 4\%$) to cPLA P20 ($E = 0.91$ GPa, $\epsilon_b = 3\%$) highlights the combined influence of microporosity and therefore PEG extraction. These values show that hierarchical porosity further decreases stiffness while only slightly affecting ductility. This suggests that microporosity, while modifying the mechanical response, has a more limited influence compared to macroporosity or PEG plasticization.

An interesting observation is that the toughness T remains nearly unchanged for Blend P20 ext. compared to cPLA P20 and even decreases for

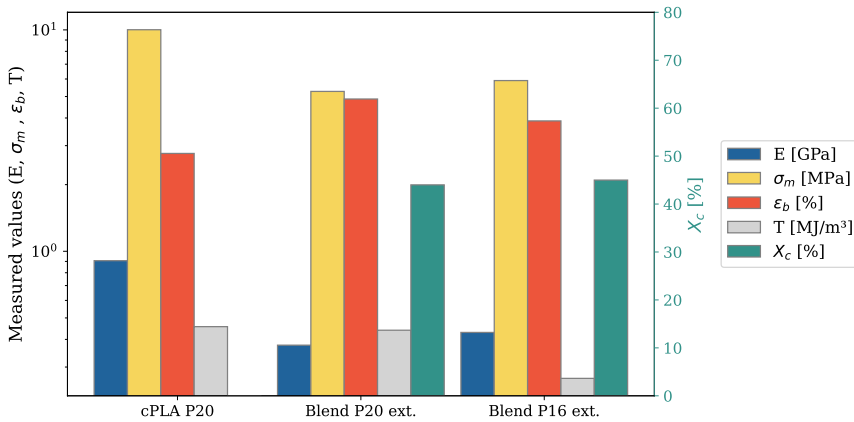


Fig. 4.6 Mechanical properties and crystallinity of hierarchically porous samples, containing both micro- and macroporosity (Blend P20 ext. and Blend P16 ext.) compared to cPLA P20 used as reference. Young's modulus (E), maximum stress (σ_m), elongation at break (ϵ_b) and area under stress-strain the curve (T) were determined from tensile tests. Crystallinity (X_c) was determined from DSC measurement carried out on the samples after the mechanical testing.

Blend P16 ext. This is somewhat counterintuitive, since increased ductility often implies enhanced energy dissipation. However, the presence of micropores introduces additional stress concentration sites, which could accelerate failure initiation and offset the gains in ductility.

The presence of micropores introduces stress concentration sites that promote premature crack initiation and growth. In porous materials, deformation is not distributed uniformly, and failure may occur through localized rupture events rather than homogeneous plastic deformation. This effect is particularly pronounced in Blend P16 ext., where the combination of microporosity and macroporosity leads to a less efficient energy dissipation mechanism, reducing toughness despite increased elongation at break. However, due to the experimental variability observed, especially in toughness measurements, these conclusions must be considered with caution.

Furthermore, the persistence of stepwise failure in PLA/PEG macroporous samples after PEG extraction suggests that this phenomenon is not solely attributed to the PEG phase itself but rather to the combination of macroporosity and material heterogeneity. Prior to extraction, PEG modifies stress distribution and increases energy dissipation during deformation,

making crack propagation less abrupt. After extraction, micropores left by PEG removal further modify the local stress distribution and contribute to failure behavior. These micropores act as stress concentration points, affecting the way cracks propagate through the structure. Even though the PLA matrix regains higher stiffness after PEG extraction, the remaining porous network still disrupts crack progression, reinforcing the stepwise failure behavior. This highlights that the key factor driving this failure mode is the inhomogeneous distribution of load-bearing material in macroporous PLA/PEG structures, which disrupts uniform crack propagation and forces failure to occur incrementally.

Overall, these results confirm that while microporosity contributes to the mechanical response, its influence remains secondary to that of macroporosity. This further reinforces the conclusion that the mechanical response of porous PLA/PEG materials is primarily dictated by macroporosity, with microporosity acting as a secondary modifier rather than a dominant factor.

4.2.6 Structure–property relationships: global perspective

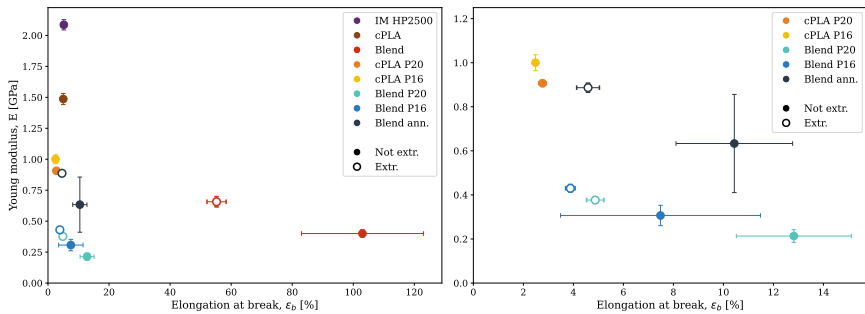


Fig. 4.7 Comparison of Young's modulus (E) and elongation at break (ϵ_b) for all samples (left), with a magnified view of the low E , low ϵ_b region (right). Solid markers represent non-extracted samples, while hollow markers correspond to extracted samples.

To provide a comprehensive overview of the mechanical behavior of all samples, the values of Young's modulus (E) and elongation at break (ϵ_b) are presented in a single graph, allowing for an easier visualization of the main mechanical trends.

As expected, in Figure 4.7 (right), the IM HP2500 sample exhibits the highest Young's modulus while maintaining a low elongation at break.

Upon 3D printing, cPLA shows a similar elongation at break but a 25% reduction in Young's modulus due to imperfections associated with additive manufacturing. Introducing macroporosity (cPLA P16 and cPLA P20) further reduces stiffness, leading to a 50% decrease in Young's modulus compared to IM HP2500, which aligns with the 50% porosity incorporated in these structures. However, the most striking effect comes from blending PLA with PEG (Blend), which induces significant plasticization, resulting in a drastic 90% reduction in Young's modulus while simultaneously increasing elongation at break by a factor of 50. Even after PEG extraction (Extr. Blend), the residual PEG within the material continues to exert its plasticizing effect and leads to an exceptional trade-off between E/ϵ_b ratio compared to other samples. Remarkably, this sample also exhibits microporosity, showing that micro-scale porosity can be introduced without compromising mechanical performance. Lastly, thermal annealing results in a slight increase in Young's modulus but this enhancement is accompanied by a sharp decrease in elongation at break, reflecting a transition toward more brittle behavior.

For clarity, the remainder of the discussion focuses on the right panel of Figure 4.7. The impact of PEG addition on macroporous samples (Blend P16 and Blend P20) is clearly visible, further reducing Young's modulus while allowing for greater deformation before failure. Even after PEG extraction, this trend is partially maintained, as seen when comparing the extracted blends (Blend P16 ext. and Blend P20 ext.) with their non-extracted cPLA P16 and cPLA P20 counterparts.

Two general trends emerge from this analysis. The first corresponds to the "reverse" effect of PEG plasticization after its extraction. For all samples, their extracted counterparts systematically exhibit a higher Young's modulus and a lower elongation at break, confirming the stiffening effect of PEG removal. The second trend is related to macroporosity morphology, where structures with smaller unit cells (P16) result in a stiffer material (higher E) but also a higher ϵ_b compared to P20, as previously discussed.

4.2.7 Conclusions

The mechanical performance of PLA/PEG-based structures is intricately linked to the presence and the scale of the porosity; microporosity which arises from the extraction of PEG and the macroporosity induced by the 3D printing process. Microporosity seems to only have a slight effect on

the mechanical properties. Even after extraction, PEG continues to exert a plasticizing effect, as a fraction of it remains embedded within the PLA matrix. This residual PEG likely contributes to the mechanical performance of the material by preserving local chain mobility and mitigating brittleness. This effect is particularly evident in the extracted blend sample, which incorporates microporosity while presenting a great trade-off regarding Young's modulus and elongation at break.

In contrast, the macroporosity introduced by 3D printing has a considerably more detrimental effect on mechanical properties. This is clearly illustrated by the P16 and P20 samples, which both exhibit low Young's modulus and limited elongation at break, indicating poor mechanical resilience. These specimens were fabricated using a gyroid-based architecture designed to induce periodic macroporosity. While such macroporosity can be tailored through geometric parameters—including cell size and wall thickness, often expressed as the ratio t/l , the current results suggest that insufficient structural support within the printed network severely compromises mechanical integrity. Notably, P16 outperforms P20, likely due to a higher wall-to-cell ratio, which provides improved load distribution and enhanced stiffness. Nevertheless, both P16 and P20, especially after PEG extraction, remain substantially weaker than the extracted blend sample, where only microporosity is present. This comparison underscores that while microporosity arising from PEG removal does not markedly deteriorate mechanical performance, macroporosity introduces structural discontinuities that dominate the mechanical response and lead to premature failure.

Despite these challenges, the behavior of the extracted blend sample offers a promising future for the development of hierarchically porous materials. It demonstrates that it is indeed feasible to introduce microporosity via PEG extraction while preserving mechanical robustness, provided the macroporous design is precisely controlled and optimized. These insights highlight the potential to fabricate advanced scaffolds that combine interconnected porosity with sufficient mechanical integrity to maintain structural support during tissue regeneration.

PART V

Conclusions and prospects

1

Conclusion

The goal of this thesis was to develop a simple and robust strategy for fabricating biomaterials with hierarchical porosity using only accessible FDA-approved polymers and processing methods, in order to facilitate on-site implementation in the context of personalized medicine. This work focused on PLA and PEG, two semi-miscible polymers, and how their crystallization behavior and phase interactions could be exploited to generate multi-scale porosity. In particular, the control of PLA crystallization and the construction of an experimental phase diagram enabled the prediction and tailoring of microporosity within the material. In addition, macropores were generated through FDM, contributing to the hierarchical structure by introducing porosity at the macroscopic scale. To move from fundamental understanding to practical implementation, the research was structured around five interconnected objectives, each building upon the previous to form a coherent pathway toward material design and manufacturing.

The first objective was to characterize the crystallization behavior of PLA in blends with PEG and to understand how it governs the development of microstructure. During PLA crystallization, PEG is partially excluded from the growing spherulites and accumulates in the interspherulitic regions, while another fraction remains trapped within the amorphous domains of the spherulites. This segregation mechanism results in a heterogeneous phase distribution that is particularly favorable for generating microporosity

upon PEG extraction. The extent and nature of this segregation were found to depend strongly on PEG content and molar mass. Among the compositions studied, the 70/30 PLA/PEG blend containing PEG100K provided the most favorable balance: PLA crystallized efficiently into a dense network of well-formed spherulites, while PEG was mainly retained within the amorphous phase of the spherulites forming pockets of PEG-rich phases, with a small fraction segregating to the interspherulitic regions. In contrast, at 50 wt% PEG, a larger quantity of PEG was segregated the excess PEG was entirely excluded to the interspherulitic regions, resulting in extensive void formation and material decohesion upon extraction. At the other extreme, the 10 wt% formulation resulted in over-dilution of the PEG, with most of it trapped in the interlamellar amorphous fraction of PLA inside spherulites, subsequently limiting the development of porosity. PEG molar mass also played a decisive role: higher molar mass PEG (100K and 1M) facilitated phase separation by reducing miscibility and promoting larger domain formation, whereas low molar mass (PEG3K) tended to remain more homogeneously dispersed, even at higher concentrations. Crystallization was most effective between 100°C and 110°C, a temperature range where nucleation density and spherulitic growth rate were optimally balanced.

The second objective was to experimentally determine the phase behavior of PLA/PEG blends as a function of PEG content, molar mass and temperature. This was essential to clarify the conditions under which phase separation occurs and to distinguish between liquid-liquid (LL) demixing and crystallization-induced liquid-solid (LS) phase separation. By applying extremely rapid cooling rates thanks to fDSC, it was possible to identify the state of PLA/PEG blends across a broad temperature range, from 50°C to 200°C. This approach enabled the identification of the different phases present at each temperature and their association with the corresponding phase separation mechanisms.

Four distinct regimes were identified in the phase diagram, each associated with a characteristic thermal response. Type I corresponded to fully miscible blends, typically observed above or below the crystallization temperature of PLA where no crystallization occurred. Type II was defined by the crystallization of PLA alone, without detectable PEG crystallization. This corresponds to a LS phase separation, where PLA-rich crystals formed while the amorphous regions retained a PLA/PEG mixture. This regime occurred at low PEG contents, where PEG remained finely dispersed within the amorphous phase of PLA and the resulting domains were too small and

too diluted to initiate PEG crystallization. In contrast, Type III behavior emerged in the same temperature range but at higher PEG concentrations, where both PLA and PEG were able to crystallize independently. In this case, PEG segregated into larger domains located between PLA lamellae or spherulites. A LS phase separation once again induced by PLA crystallization occurred, but with PEG-rich regions large enough to enable its own crystallization. Lastly, Type IV was associated with LL phase separation, occurring at higher temperatures close to the melting temperature of PLA. The transitions between these regimes were also strongly influenced by PEG molar mass: higher molar masses promoted earlier separation, while PEG with lower molar mass favored more homogeneous behavior. This experimentally constructed phase diagram provides a predictive tool for tuning thermal protocols and compositions to direct phase separation and morphology in PLA/PEG materials.

The third objective was to establish the link between phase separation mechanisms and the formation of porosity upon PEG extraction. It was shown that porosity emerged directly from the phase organization frozen during the crystallization of PLA. In blends where PEG was excluded from the growing PLA spherulites (Types II and III), its localization in interspherulitic or fibrillar regions created a continuous PEG-rich phase that could be selectively removed. The nature and distribution of the resulting porosity were strongly dependent on PEG content. At 30 wt%, the PEG network was sufficiently developed to form well-connected pores, while maintaining good structural cohesion of the PLA matrix. In contrast, 50 wt% PEG led to extensive voids and compromised mechanical integrity due to excessive interspherulitic PEG segregation. At low PEG content (10 wt%), the dispersed PEG domains were too small and isolated to create significant porosity after extraction. Importantly, a residual fraction of PEG, typically around 8-10 wt%, remained entrapped within the interlamellar amorphous phase of PLA and could not be removed during extraction. This residual PEG contributes to the plasticization of the matrix and provides a useful estimate of the proportion of PEG effectively involved in porosity formation.

The fourth objective was to demonstrate that the optimized PLA/PEG system could be processed via FDM to produce objects with hierarchical porosity. Filaments of the 70/30 PLA/PEG100K blend were successfully fabricated with sufficient dimensional stability and surface quality to enable consistent and homogeneous printing. Using these filaments, gyroid struc-

tures were printed, providing a regular and interconnected macroporous architecture. After printing, PEG extraction allowed the development of microporosity within the printed struts, confirming that the phase separation mechanisms observed in films were preserved during and after the extrusion step. As a result, the final object exhibited a clear hierarchical porosity at two levels: macropores defined by the printed geometry and micropores generated by PEG removal. This results validated the ability of the PLA/PEG system to be integrated into additive manufacturing workflows without additives, while achieving complex, multi-scale architectures suitable for biomedical applications.

The fifth objective was to evaluate the mechanical response of the printed blends. Tensile tests were performed on dogbone samples printed from the 70/30 PLA/PEG100K blend, in four distinct configurations: as-printed dense samples, porous samples with either microporosity (after PEG extraction) or macroporosity (gyroid structure) and samples combining both types of porosity. The addition of PEG prior to extraction led to a reduction in Young's modulus from 2.09 GPa to 0.4 GPa, accompanied by a substantial increase in elongation at break, from 5% to 100%, demonstrating the plasticizing effect of PEG. After extraction, the resulting microporous samples exhibited surprisingly good mechanical properties. A high elongation, reaching up to 55%, while partially recovering stiffness reaching a modulus of 0.66 GPa, indicating that the microporous architecture preserved ductility and mechanical integrity. In contrast, the introduction of macroporosity through the gyroid structure resulted in both low modulus and low elongation, highlighting the dominant role of macropores in weakening the mechanical properties. This trend was also observed in the samples exhibiting hierarchical porosity, where mechanical properties closely matched those of the macroporous structures alone. Finally, thermal annealing was used to induce PLA crystallization. As expected, this treatment increased Young's modulus but reduced elongation at break, indicating a transition toward more brittle behavior.

This work demonstrates that a simple PLA/PEG blend, processed under controlled thermal conditions and shaped via standard 3D printing techniques, offers a viable pathway toward the generation of hierarchical porosity, a feature of key importance in the context of personalized medicine. While the material developed in this study is not yet intended for direct biomedical application, it serves as a proof of concept that such multiscale

architectures can be achieved using accessible formulations and processing methods. In more general terms, it provides a solid basis for designing porous biomaterials by linking material composition, processing conditions and resulting in tailored properties.

2

Future prospects

While this work has demonstrated the feasibility of generating hierarchical porosity using a simple PLA/PEG system and standard processing methods, several questions remain open and multiple directions could be pursued to deepen and extend these findings. Future work should aim to optimize the formulation to balance mechanical performance and porosity, to investigate the localization and structural role of residual PEG as well as its fate upon longer time immersion in biological fluids, to better characterize how porosity influences mechanical response and degradation pathways and to improve the control over 3D printing parameters in order to enhance inter-layer cohesion and structural consistency. Additionally, efforts should be made to explore the biomedical potential of this approach by incorporating bioactive functionalities or targeting other biomedical fields such as cell culture support or drug delivery. These prospects are organized around four key areas: advanced material formulation, structure–property relationships, process optimization and biomedical functionality.

2.1 Advanced material formulation

As demonstrated through the phase diagrams established in this work, PEG molar mass has a strong influence on the miscibility with PLA and

on the nature of the resulting phase separation. This tunability represents a valuable design parameter: low-molar-mass PEGs promote miscibility and plasticization, while high-molar-mass PEGs favor phase segregation and porosity generation. In theory, this makes it possible to tailor the material's structure according to specific functional needs, from flexible and ductile materials to porous and more rigid architectures. In this context, combining PEGs of different molar masses within the same blend could offer an additional level of control: by adjusting the ratio between low- and high-molar-mass PEG, it would be possible to fine-tune the balance between plasticizing effects and phase separation, and thus modulate both the mechanical properties and the resulting porosity. However, these effects remain to be fully characterized in terms of mechanical properties and structural cohesion. Therefore an investigation across a broader range of molar masses would help clarify how this can be translated into practical performance.

Another strategy to expand the porosity range of the material would be to introduce external porogens, such as salt crystals, which can be leached out in water after processing. This could enable the formation of an additional level of macroporosity, potentially resulting in highly porous architectures with very high surface-to-volume ratios. Such structures may be particularly relevant for in vitro applications, for instance as platforms for cell expansion, where mechanical robustness is less critical than permeability and surface area. However, this approach would require careful control over porogen size and distribution and may lead to a significant reduction in mechanical strength or even the decohesion of the material. Additionally, the interaction between porogens and the FDM process would need to be assessed to ensure structural consistency during printing.

2.2 Understanding structure-property relationships

A deeper understanding of how the internal structure of the PLA/PEG material influences its behavior is essential to fully exploit its potential. One open question concerns the nature and distribution of the residual PEG that remains in the material after extraction. It is still unclear whether this PEG is totally and homogeneously dissolved in the interlamellar amorphous

domains of PLA or if a part of it is present as isolated, unconnected pockets. This distinction is not trivial, as it may affect both the mechanical integrity of the material and its interaction with biological environments. PEG-rich pockets could act as local stress concentrators, reducing the structural cohesion and promoting premature failure under mechanical load. From a biological perspective, the way PEG is distributed could also influence its evacuation from the body. Since PEG is not biodegradable, it must be eliminated in its intact form. If it is molecularly dispersed within the amorphous phase of PLA, its gradual release would likely be more manageable for the body. In contrast, if it is present in the form of isolated pockets, a burst release of a large quantity could overwhelm local clearance mechanisms and potentially trigger adverse biological responses.

In this context, identifying whether PEG is molecularly dispersed or forming nanoscopic domains in the amorphous interlamellar phase becomes critical. One indirect approach would involve small-angle X-ray scattering (SAXS), where an increase in the long period, the spacing between crystalline lamellae, would suggest swelling of the amorphous domains due to PEG incorporation. Such a shift could be interpreted as evidence for the presence of PEG chains intercalated within the non-crystalline zones of PLA. Alternatively, a more direct visualization could be achieved by selectively labeling the PEG phase with a contrast-enhancing agent, followed by ultramicrotomy and transmission electron microscopy (TEM). This technique would allow nanoscale imaging of the PLA lamellar structure and potentially reveal localized PEG accumulations, enabling a clearer distinction between homogeneous dispersion and discrete inclusions.

A more detailed analysis of the porosity would also be needed to better assess the internal structure of the material. While μ CT was used in this work to visualize the porous network, its resolution remains a limitation, particularly for detecting fine microporosity or small interconnections. As a result, the exact total porosity may be slightly misevaluated, and the functional accessibility of the pore network remains uncertain. Complementary techniques such as mercury intrusion porosimetry could help overcome these limitations by providing a more accurate estimation of the accessible pore volume across a wider range of scales, including pores below the μ CT detection threshold. In addition, the potential presence of residual PEG pockets, undetectable after extraction, could be revealed by using contrast agents that preferentially bind or dissolve in PEG prior to scanning by μ CT. This would offer a way to detect isolated inclusions and better understand

how the PEG phase is distributed and connected within the PLA matrix, both before and after extraction.

Another important avenue of investigation relates to the optimization of macroporosity. Preliminary results suggest that smaller gyroid cell sizes lead to better mechanical performance, likely due to improved stress distribution and reduced defect size. It would therefore be worthwhile to systematically reduce cell size, within the limits of the printing resolution or biological needs, to identify the optimal architecture for mechanical robustness and eventual biomedical relevance. Numerical simulations such as finite element analysis could support this optimization process by predicting stress concentrations and mechanical failure zones across different pore geometries, helping to identify the most mechanically favorable architectures before fabrication.

Finally, the degradation behavior of the material remains to be fully characterized. The high surface-to-volume ratio introduced by the hierarchical porosity is expected to accelerate degradation but the mode of degradation, homogeneous erosion versus localized fragmentation, remains unknown. This has important implications for long-term performance, particularly if the amorphous regions degrade faster than the crystalline domains, potentially leading to loss of cohesion. In this context, crystallinity itself could be used as a design parameter to modulate degradation rates: higher crystallinity may slow degradation by stabilizing the structure, while a more amorphous matrix could promote faster resorption. Understanding how crystallinity and porosity together influence degradation kinetics would be critical for applications requiring controlled resorption or drug release.

2.3 Process optimization

Although the PLA/PEG blend demonstrated good printability using standard fused deposition modeling, further improvements are needed to enhance layer-to-layer adhesion. Limited cohesion between printed layers is a well-known constraint in FDM and is expected to significantly affect the mechanical performance of porous structures. Strategies such as increasing nozzle temperature, printing speed, or layer thickness could help promote

polymer diffusion and improve bonding. Another promising approach is thermal annealing of the printed parts at a temperature between the glass transition and crystallization temperatures of PLA. This would activate chain mobility and reinforce interlayer fusion without drastically altering the internal phase structure. However, in the presence of PEG, the thermal window must be carefully chosen, as exceeding the PEG melting point could lead to unwanted reorganization.

Additionally, the orientation of the printed object relative to the loading direction can significantly affect mechanical properties. Since layer boundaries generally represent mechanically weaker zones, misalignment with the principal stress axis may lead to premature failure along these planes. In porous materials, this effect may be amplified by the reduced cross-sectional area and local stress concentrations, making printing orientation a critical factor to consider in mechanical design.

2.4 Toward biomedical functionality

While this work focused on the physical generation of hierarchical porosity, future efforts should move toward adapting the material for biomedical use. In the context of bone tissue regeneration, in particular, one important step would be to enhance its biocompatibility by incorporating bioactive fillers such as hydroxyapatite. Dispersing such particles into the PEG phase before blending could allow their homogeneous redistribution throughout the PLA matrix after PEG extraction. This strategy could improve both cellular response and mechanical properties by increasing stiffness and promoting osteoconductivity.

A completely different direction could also be envisioned by repurposing the PLA/PEG system for drug delivery applications. While this thesis focused on structural design and porosity control, the same material system could be leveraged for controlled release strategies with biomedical relevance. Two main approaches could be considered. In the first, the porous PLA matrix, after PEG extraction, is used as an inert reservoir that can be loaded with therapeutic agents. The interconnected pore network then enables diffusion-based release, offering a passive but potentially sustained

delivery system. In the second approach, bioactive molecules are incorporated into the PEG phase before blending. Once implanted, the PEG dissolves gradually within the body, triggering the release of the embedded agents. This strategy allows the release profile to be tuned via PEG content, molar mass, and phase distribution. However, the biological impact of PEG dissolution must be carefully considered, particularly if the polymer is released fast and in large quantities.

These developments would transition the material from a structural proof of concept toward a multifunctional system adapted to biomedical applications. By integrating bioactive components or enabling controlled release, the PLA/PEG platform could be tailored to meet the specific requirements of tissue regeneration, local drug delivery or in vitro cell culture. These adaptations would represent an important step toward translating the material into practical biomedical use.

PART VI

Annexes

1

Validation of Isothermal Equilibrium Time

1.1 Isothermal equilibrium during fDSC experiments

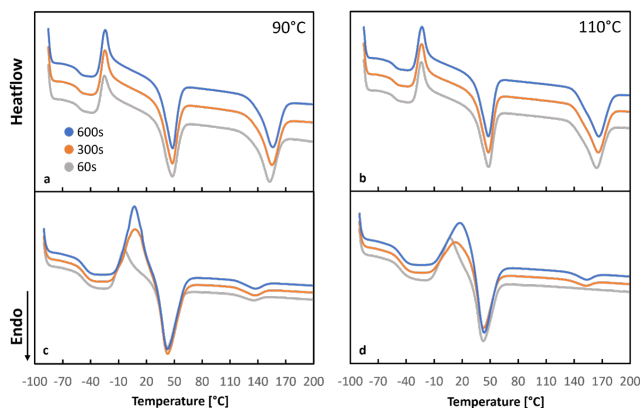


Fig. 1.1 fDSC heating curves of PLA/PEG1M 50/50 (a, b) and PLA/PEG3K 50/50 (c, d) after isothermal treatment at 90°C (left) and 110°C (right) for durations of 60s (grey), 300s (orange) and 600s (blue).

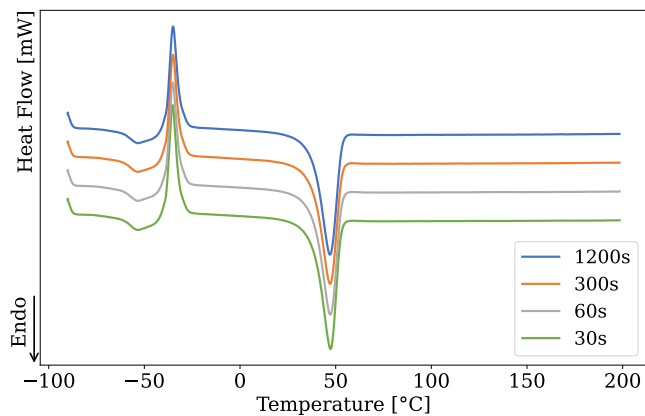


Fig. 1.2 fDSC heating curves of PLA/PEG100K 70/30 after isothermal treatment at 180°C for durations of 30s (green), 60s (grey), 300s (orange) and 1200s (blue).

1.2 Isothermal equilibrium during LL phase separation

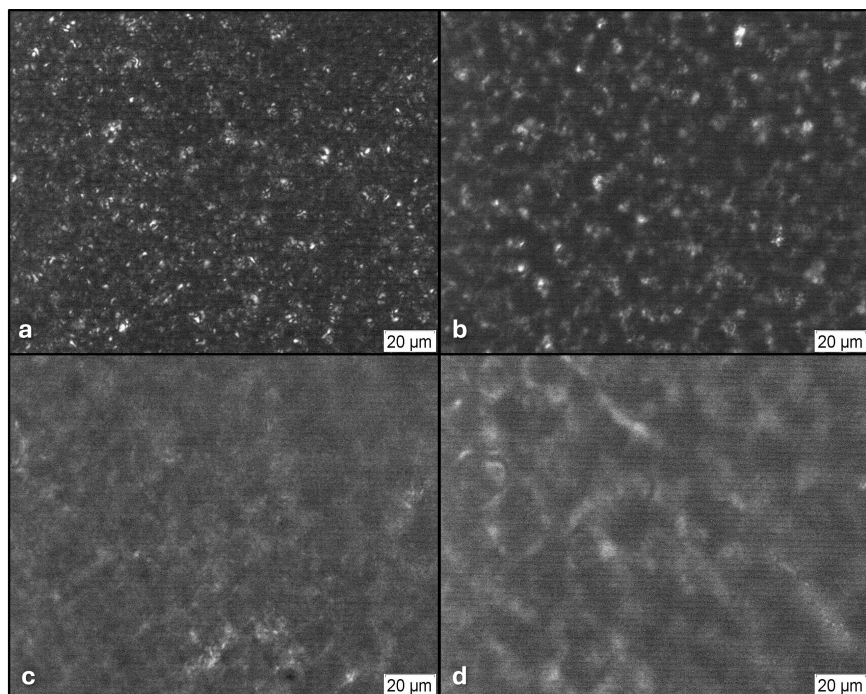


Fig. 1.3 POM images of PLA/PEG100K 70/30 films maintained at 200°C for 5 minutes (a,c) and 20 minutes (b,d), then immediately quenched in liquid nitrogen. Each sample is shown before (a,b) and after (c,d) PEG extraction. The disappearance of birefringent domains after PEG removal indicates that the observed crystalline structures correspond to PEG crystals, further supporting the occurrence of phase separation prior to quenching

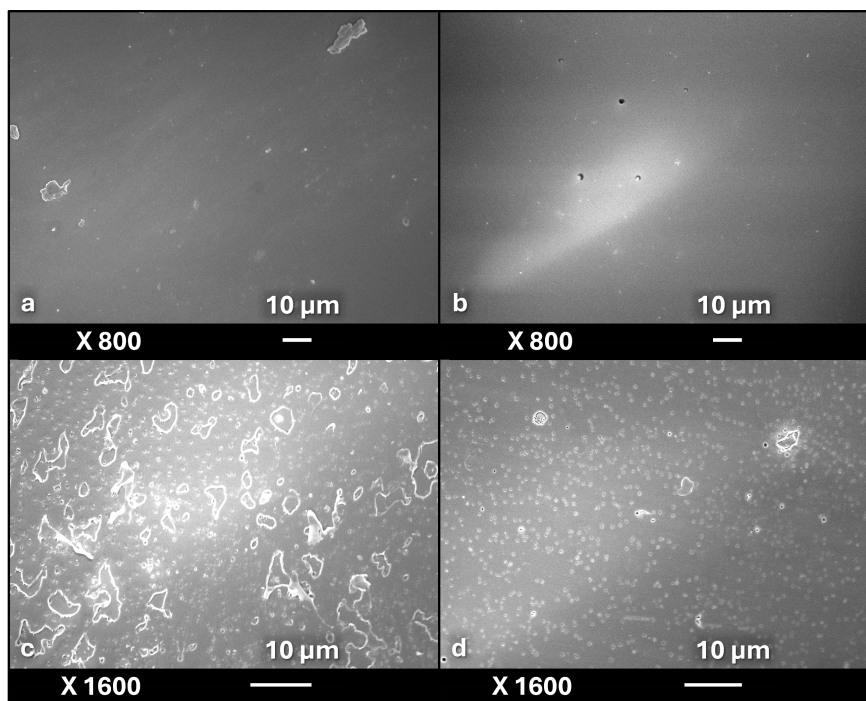


Fig. 1.4 SEM images of PLA/PEG100K 70/30 films maintained at 200°C for 5 minutes (a,c) and 20 minutes (b,d), then immediately quenched in liquid nitrogen. Each sample is shown before (a,b) and after (c,d) PEG extraction. The appearance of pores following PEG removal confirms the occurrence of a liquid–liquid phase separation via a binodal demixing pathway.

2

Stress-strain curves of mechanical tests

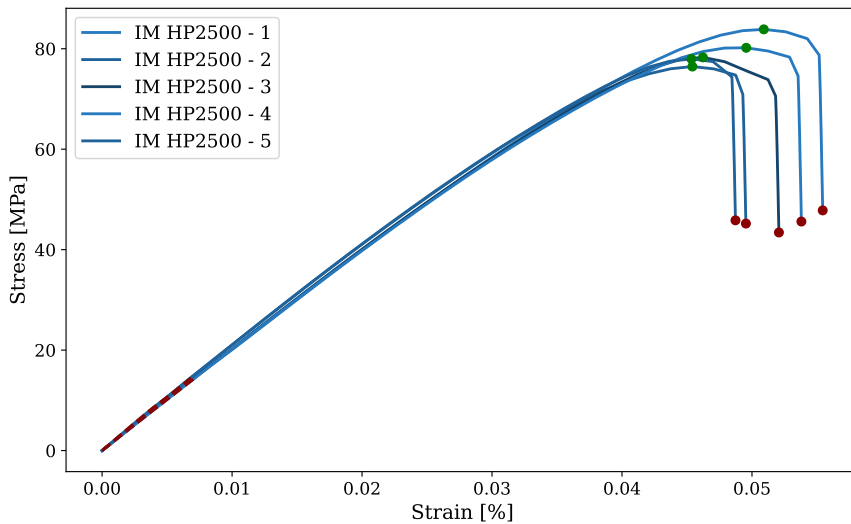


Fig. 2.1 Stress-strain curve of IM HP2500 sample from tensile test. E , σ_m and ϵ_b of each curve are represented by the red dotted line, green dot and red dot, respectively.

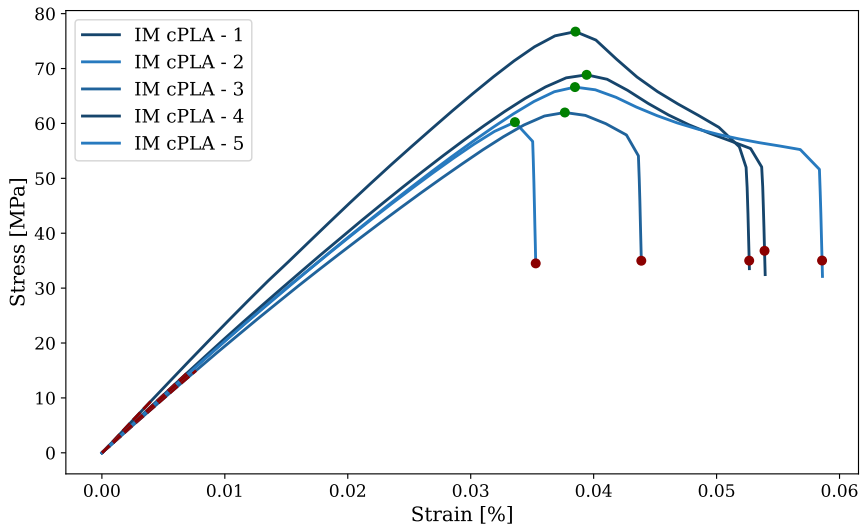


Fig. 2.2 Stress-strain curve of IM cPLA sample from tensile test. E , σ_m and ϵ_b of each curve are represented by the red dotted line, green dot and red dot, respectively.

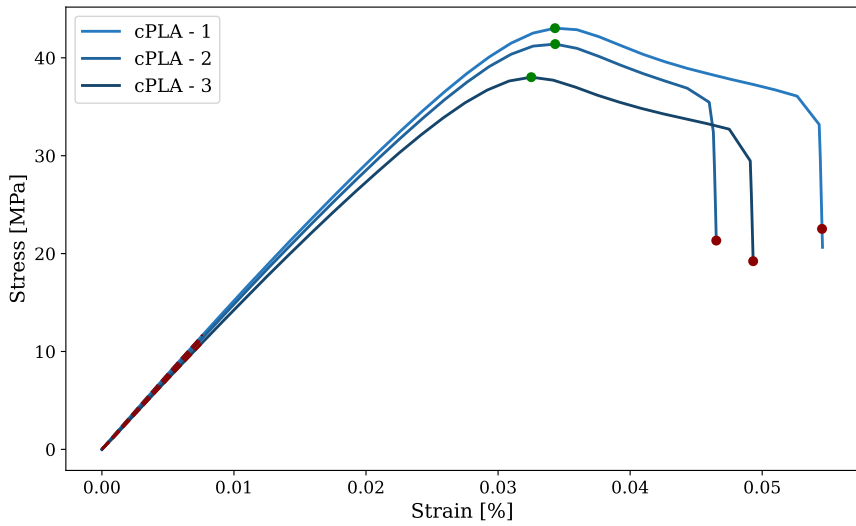


Fig. 2.3 Stress-strain curve of cPLA sample from tensile test. E , σ_m and ϵ_b of each curve are represented by the red dotted line, green dot and red dot, respectively.

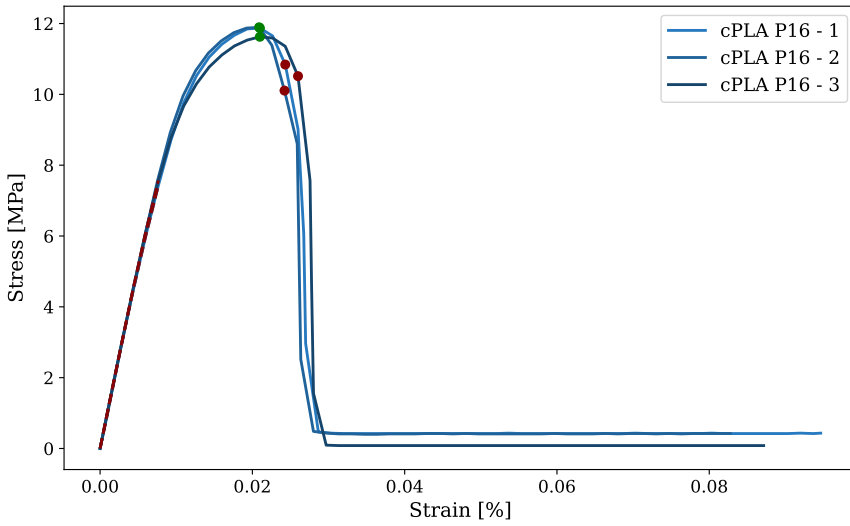


Fig. 2.4 Stress-strain curve of cPLA P16 sample from tensile test. E , σ_m and ϵ_b of each curve are represented by the red dotted line, green dot and red dot, respectively.

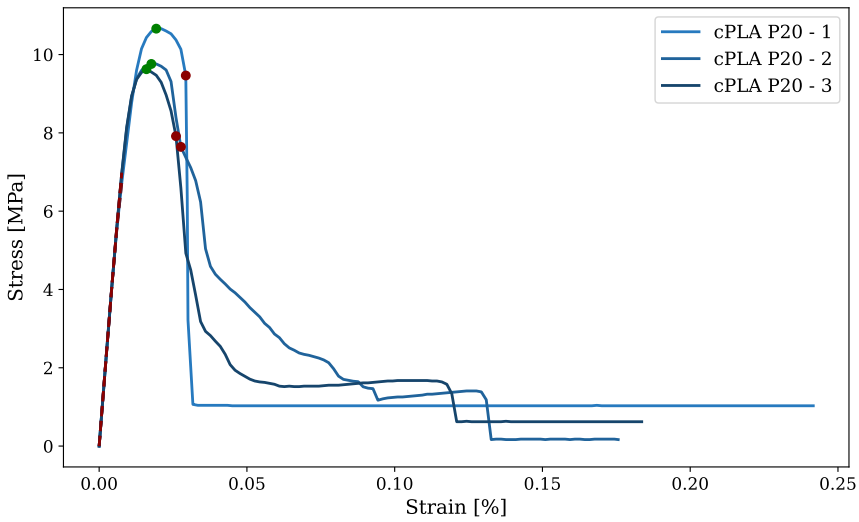


Fig. 2.5 Stress-strain curve of cPLA P20 sample from tensile test. E , σ_m and ϵ_b of each curve are represented by the red dotted line, green dot and red dot, respectively.

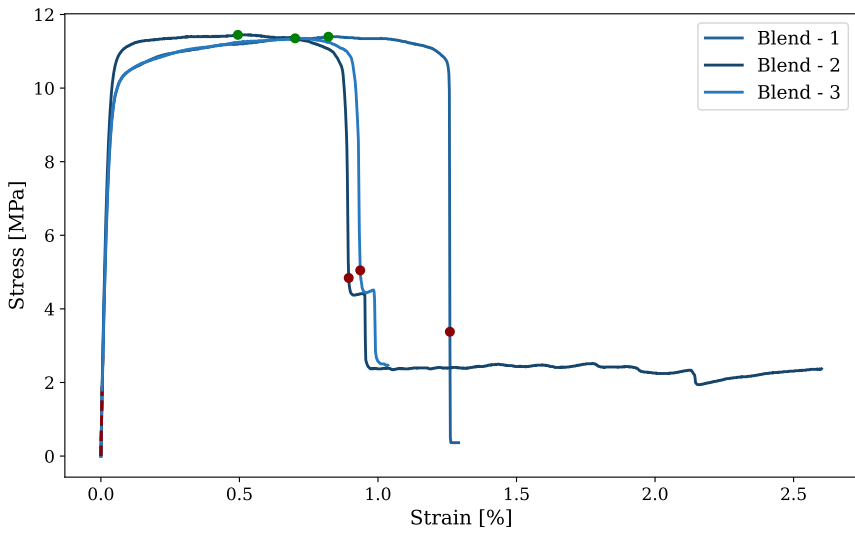


Fig. 2.6 Stress-strain curve of Blend sample from tensile test. E , σ_m and ϵ_b of each curve are represented by the red dotted line, green dot and red dot, respectively.

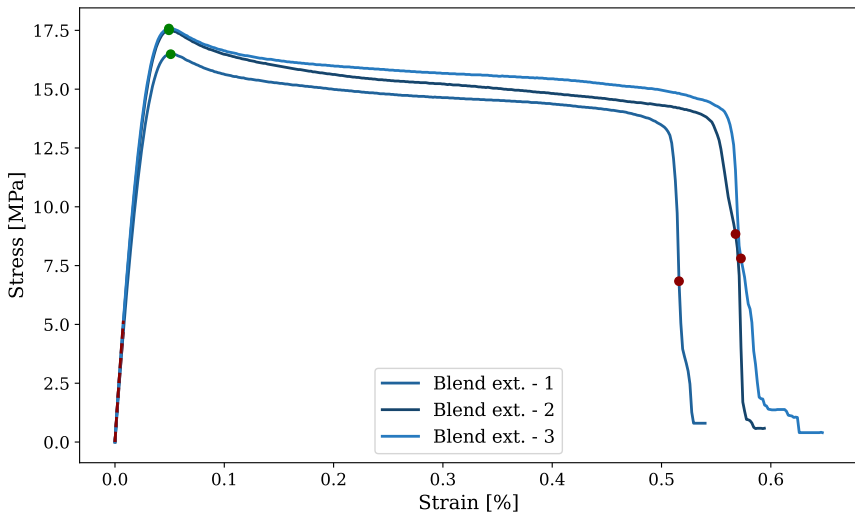


Fig. 2.7 Stress-strain curve of Blend ext. sample from tensile test. E , σ_m and ϵ_b of each curve are represented by the red dotted line, green dot and red dot, respectively.

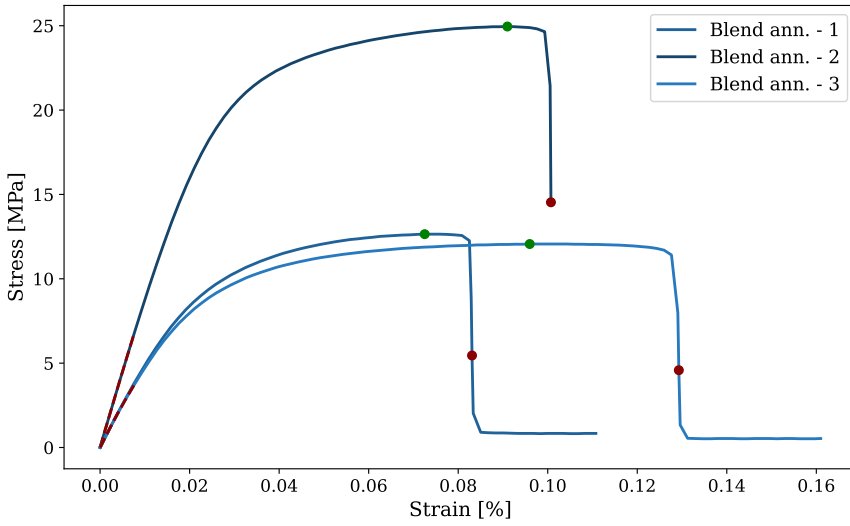


Fig. 2.8 Stress-strain curve of Blend ann. sample from tensile test. E , σ_m and ϵ_b of each curve are represented by the red dotted line, green dot and red dot, respectively.

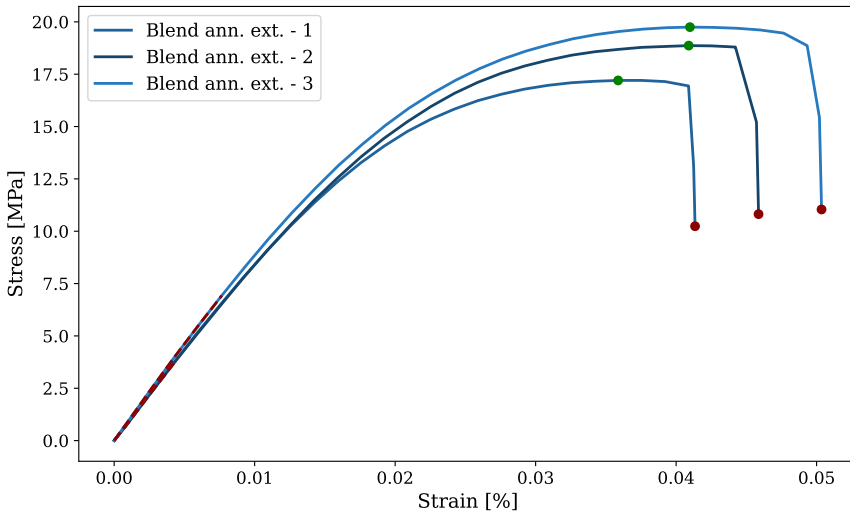


Fig. 2.9 Stress-strain curve of Blend ann. ext. sample from tensile test. E , σ_m and ϵ_b of each curve are represented by the red dotted line, green dot and red dot, respectively.

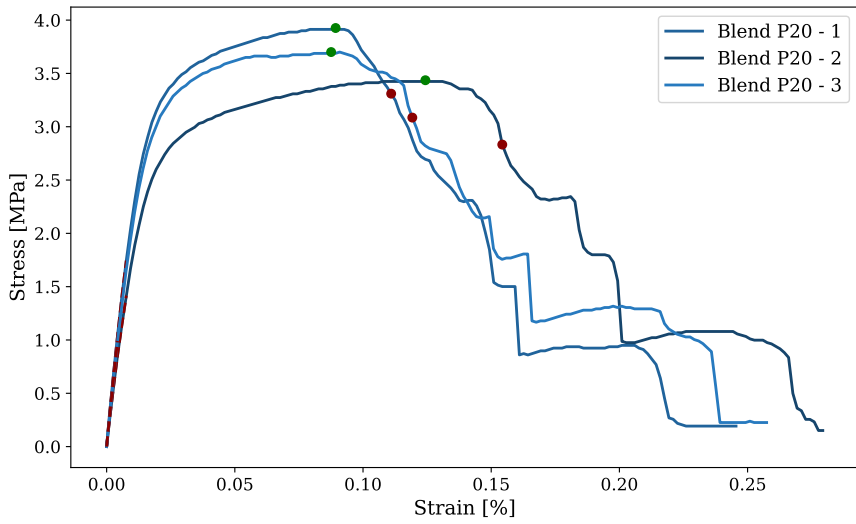


Fig. 2.10 Stress-strain curve of Blend P20 sample from tensile test. E , σ_m and ϵ_b of each curve are represented by the red dotted line, green dot and red dot, respectively.

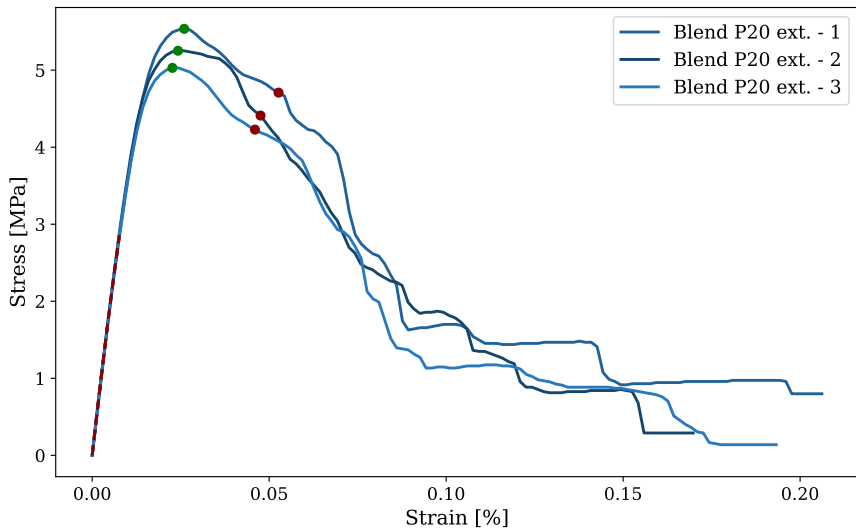


Fig. 2.11 Stress-strain curve of Blend P20 ext. sample from tensile test. E , σ_m and ϵ_b of each curve are represented by the red dotted line, green dot and red dot, respectively.

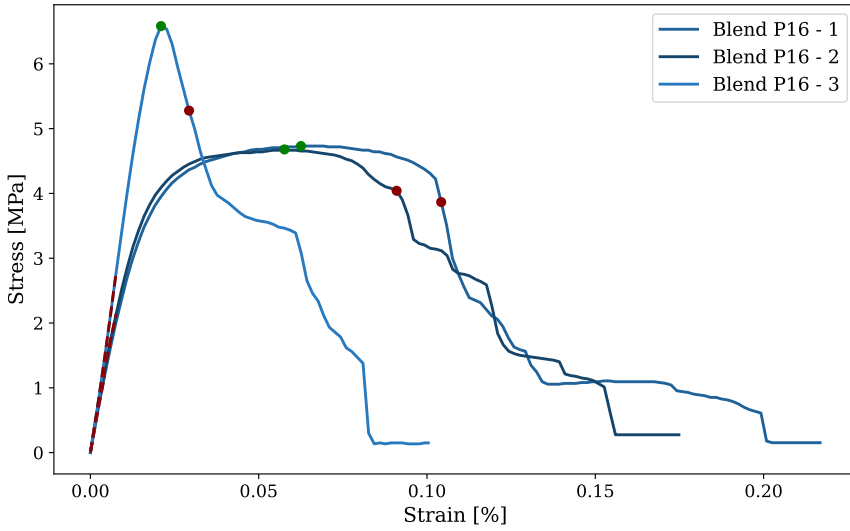


Fig. 2.12 Stress-strain curve of Blend P16 sample from tensile test. E , σ_m and ϵ_b of each curve are represented by the red dotted line, green dot and red dot, respectively.

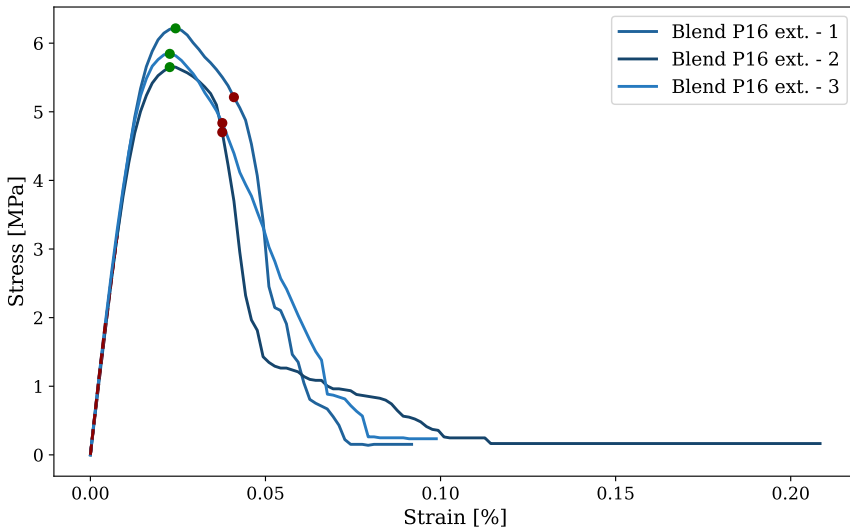


Fig. 2.13 Stress-strain curve of Blend P16 ext. sample from tensile test. E , σ_m and ϵ_b of each curve are represented by the red dotted line, green dot and red dot, respectively.

3

DSC curves of dogbone specimens after tensile test

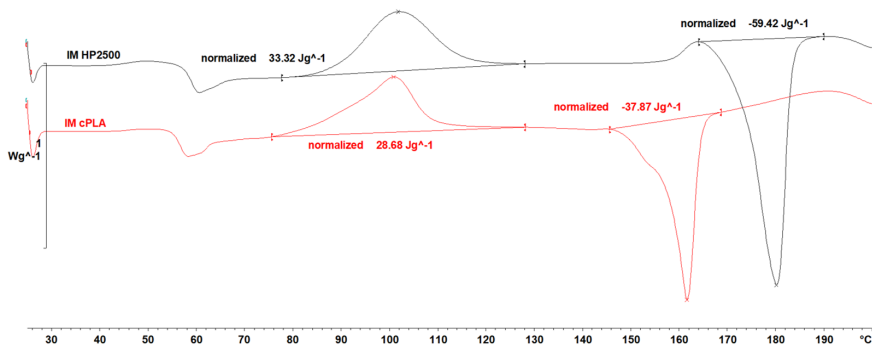


Fig. 3.1 Average DSC curves of IM HP2500 and IM cPLA used for the crystallinity determination after tensile test.

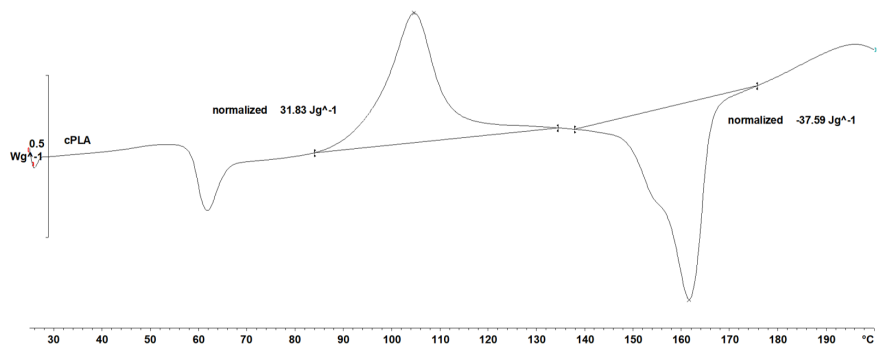


Fig. 3.2 Average DSC curves of cPLA used for the crystallinity determination after tensile test.

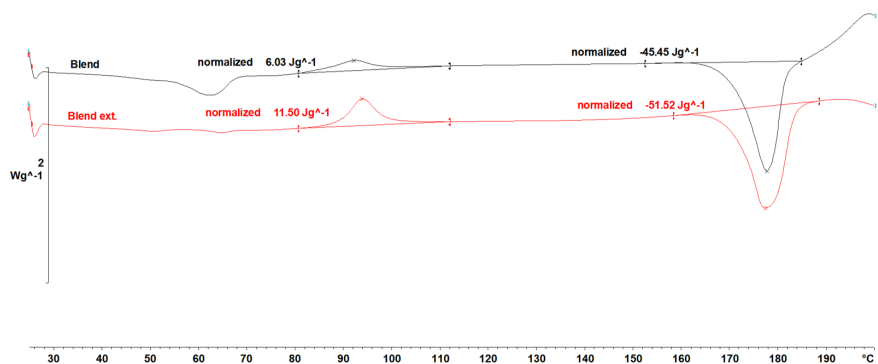


Fig. 3.3 Average DSC curves of Blend and Blend ext. used for the crystallinity determination after tensile test.

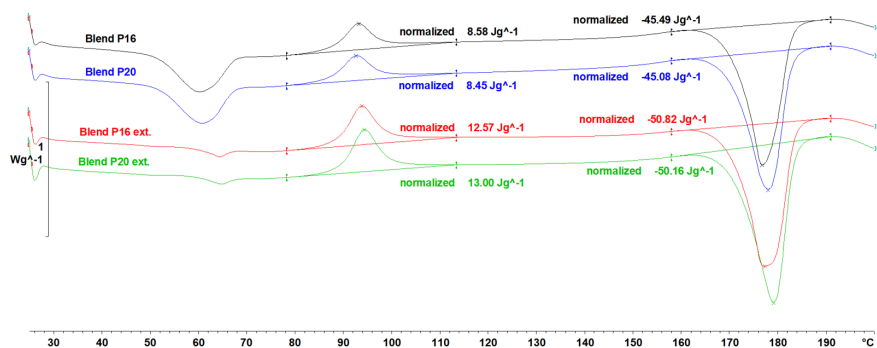


Fig. 3.4 Average DSC curves of Blend P16, Blend P20, Blend P16 ext. and Blend P20 ext. used for the crystallinity determination after tensile test.

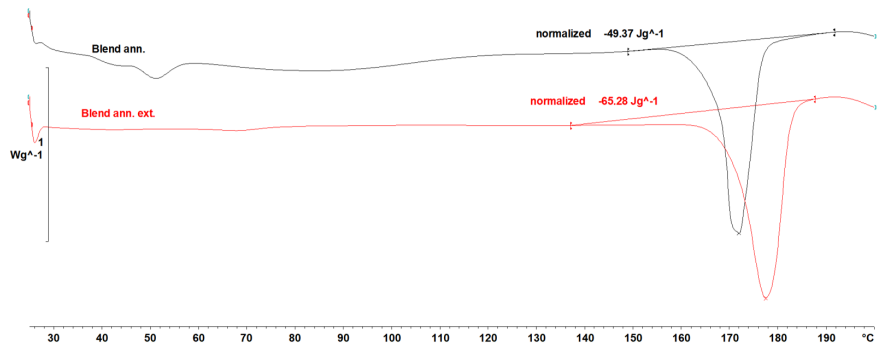


Fig. 3.5 Average DSC curves of Blend ann. and Blend ann. ext. used for the crystallinity determination after tensile test.

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