



UNIVERSITÀ DEGLI STUDI DI NAPOLI
FEDERICO II

**DI
C
Ma
PI**
Dipartimento
di Ingegneria Chimica,
dei Materiali e della
Produzione Industriale
Università degli Studi
di Napoli Federico II



**Scuola Politecnica e
delle Scienze di Base**



Università degli Studi di Napoli Federico II
Ph.D. Program in Industrial Products and Processes Engineering
XXXVII Cycle

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

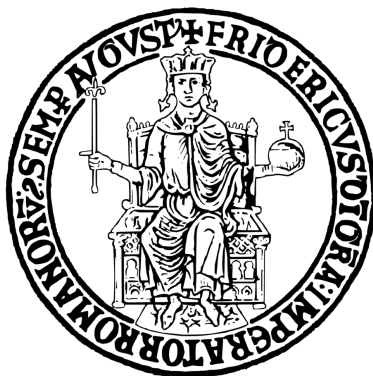
LORENZO MIELE

Micro and Nano Structuring of Soft Composite Film for Optoelectronics

Advisors:

Prof. Ernesto Di Maio

Prof. Antonio Abate



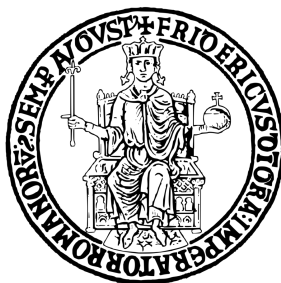
SCUOLA POLITECNICA E DELLE SCIENZE DI BASE
DIPARTIMENTO DI INGEGNERIA CHIMICA, DEI MATERIALI E DELLA PRODUZIONE INDUSTRIALE

MICRO AND NANO STRUCTURING OF SOFT COMPOSITE FILM FOR OPTOELECTRONICS

Ph.D. Thesis presented
for the fulfillment of the Degree of Doctor of Philosophy
in Industrial Products and Processes Engineering
by

LORENZO MIELE

October 2024



Approved as to style and content by
Prof. Ernesto Di Maio, Prof. Antonio Abate

Università degli Studi di Napoli Federico II
Ph.D. Program in Industrial Products and Processes Engineering
XXXVII cycle - Chairman: Prof. Andrea D'Anna

Candidate's declaration

I hereby declare that this thesis submitted to obtain the academic degree of Philosophiæ Doctor (Ph.D.) in Industrial Products and Processes Engineering is my own unaided work, that I have not used other than the sources indicated, and that all direct and indirect sources are acknowledged as references.

Parts of this dissertation have been published in international journals and/or conference articles.

Napoli, December 10, 2024

A handwritten signature in black ink, reading "Lorenzo Miele". The signature is written in a cursive style with a horizontal line underneath it.

Lorenzo Miele

Abstract

Keywords: Morphology, Polymer, Perovskite, Foam, Bubble.

This thesis centers on the study and the design of novel approaches for the structuring of polymeric composite films on the micro and nano scales fabricated through phase separation processes. We investigated the mechanisms that governs the morphology build up of a dispersed phase within a polymeric matrix enhancing the scientific comprehension and thus developing novel processing tools. Two systems were analyzed, namely polymeric porous membranes, and a tin-based perovskite-polymer composite.

The gas foaming technique is a facile and scalable method for production of pores/bubbles in a polymeric matrix. We considered different strategies to tailor the bubbles morphology exploiting the effect of process parameters, in particular the blowing agent and pressure. The use of a blowing agent in its liquid state has been explored, exploiting its transition to the gaseous phase to impose a non-trivial pressure drop reduction. Considering the effect of pressure, we propose the use of non-trivial pressure treatment, named *inverse pressure quench*, designed to manipulate the bubble dynamics. In particular, by releasing the pressure to an intermediate pressure, it is possible to reduce the bubble growth and prevent impingement, thus gaining a tool for studying phenomena involved in polymer foaming and, more generally, in polymer physics. We studied the model PP/N₂ system, and observed bubble growth, Ostwald ripening of close bubbles, bubble interaction causing shape change (from spherical to polyhedral and *vice versa*) up to coalescence, various bubble growth regimes, and bubble relative position variation due to periodic pressure histories. Our method deepens the study of fundamental processes involved in foaming and their application in structuring polymeric materials.

Moving towards the applications, this study investigates the use of physical foaming techniques for the fabrication of porous polymeric membranes with nanometric thickness from poly(lactic-co-glycolic) acid (PLGA) thin films. Employing a gas-impermeable barrier layer, we successfully impeded gas diffusion out from the sample, forcing the cellular structure formation. The results highlight the impact of nanoscale confinement on morphology and the procurance of early coalescence. Thus, we propose the so called *Coarsening Driven Gas Foaming* technique, which consists in controlling the cells coarsening as a tool to produce larger, open cells, without compromising film stability.

The thesis then extends its attention to tin halide perovskite films for solar cell application, emphasizing the need for morphological control of the crystals structure to enhance optoelectronic quality and long-term stability. We showed that the addition of a pyridine-based polymeric additive can slow down the crystallization process, leading to the formation of crystals encapsulated in a polymeric matrix, namely a perovskite-polymer composite film. Finally, the combination of the pyridine-based polymer with the corresponding small molecule enabled adjustment of the crystallization process, while keeping the polymer content minimal, facilitating electrical transport between the perovskite grains and proving effective in enhancing the power conversion efficiency of the solar cell perovskite devices.

This research deepens the analysis of mechanisms driving morphology build up during phase separation process. By leveraging the study and engineering of different systems, resulting in innovative processing tools that open new avenues for fabrication of structured materials.

Contents

Abstract	i
1 Introduction	1
1.1 Introduction	1
1.1.1 Polymer physical foaming	2
1.1.2 Strategies for bubble morphology control in poly- meric foams	3
1.1.3 Tin based perovskite solar cell	6
1.1.4 Solution processing perovskite thin film	7
1.1.5 Strategies for perovskite crystals morphology control	7
1.2 Aim of the study	12
2 Liquid foaming of Thermoplastic Polyurethane with Methy- lal	15
2.1 Introduction	15
2.2 Materials and Methods	20
2.2.1 Materials	20
2.2.2 Experimental setup	20
2.2.3 Liquid and gas foaming experiments	21
2.2.4 Pressure drop rate measurement	23
2.2.5 Liquid-vapour equilibrium Methylal	23

2.2.6	TPU foam characterization	25
2.2.7	Solubility and swelling measurements	26
2.3	Results and discussion	26
2.3.1	Liquid-vapor equilibrium Methylal	27
2.3.2	Solubility and Swelling	27
2.3.3	Pressure drop history	29
2.3.4	Liquid-vapor foaming	31
2.3.5	Liquid foaming	31
2.3.6	Gas foaming with Methylal as a co-blowing agent . .	35
2.4	Conclusions	38
3	Bubble dynamic manipulation in polymeric foaming	39
3.1	Introduction	39
3.2	Materials and Methods	40
3.2.1	Materials	40
3.2.2	Visual observation apparatus	41
3.2.3	Image analysis	42
3.3	Results and Discussion	43
3.3.1	Bubble number density	43
3.3.2	Bubble growth manipulation	44
3.3.3	Periodic treatment	59
3.4	Conclusions	61
4	Porous membranes produced via physical foaming	63
4.1	Introduction	63
4.2	Materials and methods	65
4.2.1	Materials	65
4.2.2	Film preparation	65
4.2.3	Porous membranes fabrication via physical foaming .	65
4.3	Results and discussion	66
4.3.1	Diffusion restricted physical foaming	66

4.3.2	Morphology characterization	69
4.3.3	Coarsening driven physical foaming	71
4.4	Conclusions	73
5	Polymer assisted tin-based perovskite formation for optoelectronics	75
5.1	Introduction	75
5.2	Materials and methods	76
5.2.1	Materials	76
5.2.2	Perovskite precursor solution preparation	77
5.2.3	Device fabrication	77
5.2.4	Characterizations and measurements	78
5.3	Results and discussion	79
5.3.1	Polymer perovskite compatibility	79
5.3.2	Film deposition process	80
5.3.3	Crystal structure	83
5.3.4	Morphology characterization	85
5.3.5	Device performance	88
5.4	Conclusions	90
6	Conclusions	93
A	Bubble dynamic manipulation in polymer foaming	97
A.1	Rheological measurements	97
B	Porous membranes produced via physical foaming	99
B.1	Spin coating parameter optimization	99
B.2	Film thickness measurement	99
	List of Figures	103
	Bibliography	109

Chapter 1

Introduction

1.1 Introduction

Phase separation from a single-phase mixture is exploited for the production of a wide range of structured materials, such as foams [1], polymeric membranes [2], semiconductors [3], liquid crystals [4], and nanocomposites [5]. When an homogeneous phase becomes metastable, the sequence of events that characterize the formation of a new phases, regardless its physical state, is: (i) nucleation, which is the formation of small stable particles of the new phase, called nuclei [6, 7, 8], (ii) growth, where these nuclei expand [9, 1], (iii) and coarsening. The latter involves the coalescence, when neighboring particles or bubbles merge [10], and the Ostwald ripening, when smaller particles dissolves in favor of the growth of larger ones [11, 12]. Although classical phase separation theory qualitatively describes different systems, each phase separation process is different according to the specific nature of the materials involved (e.g. liquid-gas, liquid-solid, liquid-liquid, ...). In fact, in each case a different phase formation step limits or drives the overall process and a proper description is required. For example, in liquid-gas systems, a primary objective is to maintain the structure established during bubble nucleation and growth, which is undermined by the easy occurrence of bubble coalescence, which inevitably leads to structural collapse [13, 14]. On the contrary, in the precipitation of a solid phase from a liquid solution, the coarsening step is very slow and often requires energy to occur within a reasonable processing time [15]. The growth stage is also peculiar in the case of solid phase formation (different for a gaseous phase), as it is affected by the lattice

constraints that govern the ordering of atoms according to the Wulff construction, which make the growth directional in preferred crystallographic orientation [16, 17, 18]. These specific aspects, related to the nature of each phase, consequently influence the design of the phase separation based processes. In some cases, certain phenomena are minimized or completely suppressed, in other cases they are emphasized in order to accelerate the kinetics of the limiting steps, thus maximizing their effect in structuring the material. The possibility of enhancing and refining the nowadays established processes can allow for the fabrication of advanced products, as well as making the novel design process more repeatable, simple and scalable. This requires a deeper understanding of the phenomena governing the phase separation with respect to each system along with new inspirations. In this context, the study of apparently different systems, based on the same (or similar) governing rules, proves fundamentals in developing novel processing tools.

1.1.1 Polymer physical foaming

Polymer physical foaming is a scalable, efficient and versatile technology that is widely used to produce lightweight, porous polymeric materials [1] used in consumer and industrial products such as packaging, thermal insulation, impact protection, cushioning and sporting goods [19, 20, 21]. Moreover, this approach is gaining interest due to its environmental advantages over chemical foaming techniques, along with the capacity to adjust the process to customize the final product properties by tailoring the bubble morphology [20]. Among the different technologies to produce a polymeric foam by physical foaming, namely extrusion [22], injection moulding [23], and steam chest moulding [24], the batch foaming is the appropriate technique to study and develop novel processes and processing tools. It is mainly used for research purposes on a laboratory scale, it is versatile and easy to adapt and allows a fine control of the processing variables [1, 25, 26]. This process involves the dissolution of a physical blowing agent (BA) in a polymer matrix, forming a polymer/BA solution, then, by creating a thermodynamic instability, the dissolved gas separates forming bubbles or diffuses out from the polymer matrix. In details the Batch foaming process proceeds as follows: (i) dissolution of the blowing agent (BA) at high pressure (ii) fast depressurization that bring the system

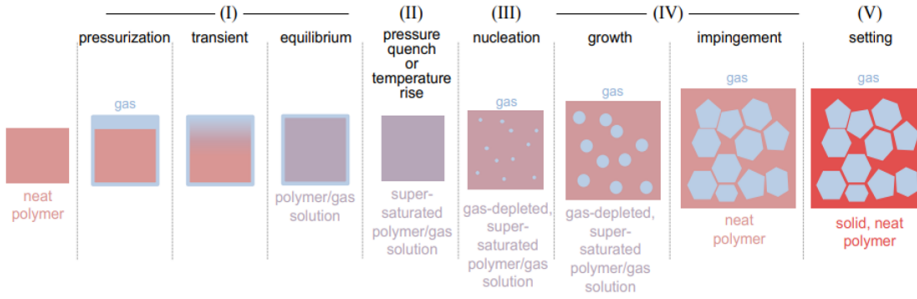


Figure 1.1. Processing stages of a typical physical foaming processes. Reproduced with permission [1]. Copyright©2021 Elsevier B.V.

into an over-saturated state (iii) phase separation through nucleation and growth of the bubbles into the polymer matrix (iv) setting of the foamed structure [1] as schematically described in Figure 1.1.

The formation of the polymer/BA solution basically depends on the diffusivity and solubility of the BA with respect to the polymer, which depends on the molecular architecture and on the chain configuration and interactions of the polymer and the BA [27]. The bubbles formation process, from their nucleation to growth and setting, is more complex and involves the rheological, interfacial and thermal properties of the system [28, 29, 30, 31, 32]. These suggest the main processing parameters, which are temperature, which primarily affects the system viscosity, pressure [1], which regulates the BA concentration, pressure drop reduction and the type of BA, which mainly affect the nucleation step [33, 27]. In Chapters 2 and 3, an in-depth analysis of the effect of foaming parameters and the physics governing the physical foaming is carried out. Eventually new strategies and novel approaches are presented.

1.1.2 Strategies for bubble morphology control in polymeric foams

The physical foaming technique has the potential to broaden its range of applications, considering the production of biomedical scaffolds [34],

filtration membranes [2], drug delivery systems [35], photonic devices [36], and templating supports [37]. The main limitation is the need for a very precise tailoring of the bubble morphology, in terms of bubble number density, bubble size and bubble size distribution, bubble shape, spatial distribution and structural characteristic, as depicted in [Figure 1.2](#).

Several strategies are reported in the literature to control the bubble morphology produced via physical foaming, from the easiest to the most complex ones. Simple modulation of the main process parameters, such as temperature, pressure, pressure drop rate and BA type, allows a facile adjustment of the product density and of the number of bubbles and the mean size [1, 40, 41, 27]. Although the tuning of these parameters is very effective, they do not allow a fine control, and novel strategies, considering the simultaneous effect of multiple parameters, as well as a complex variation of the single ones, have been proposed.

The simultaneous use of multiple blowing agents is a promising approach for controlling the bubble number density, size, and size distribution [41, 42, 43]. For example, the effect of CO₂ and N₂ together promotes bubble growth and nucleation respectively, allowing refinement of the final morphology [27]. Additionally, strategies to produce a bimodal size distribution of bubbles were presented in literature. Cheng et al. [44] produced polymeric foams with bimodal cell distribution leveraging the heterogeneous nucleation effect of nano-particles, while, Ma et al. [45] employed a two-step pressure reduction process to produce bimodal polycarbonate (PC) foams with both small and large cells.

Among the pores spatial distribution control strategies stands the so-called "graded technology", firstly proposed by Trofa. et al. [46] in which a local morphology control is obtained by imposing a non-equilibrium concentration profile of blowing agent. This technique is very effective in controlling the spatial distribution of bubbles, especially with respect to the mechanical properties of the final products [47, 48].

The morphology control achieved by these techniques is not enough precise, in fact the bubble size distribution remains coarse, lacking in a detailed control over each single bubble and structural characteristics (i.e. bubble relative position, ordering), making the aforementioned approaches not sufficiently advanced for the previously mentioned applications. Furthermore, when considering nano-structured systems, such as nanoparticles,

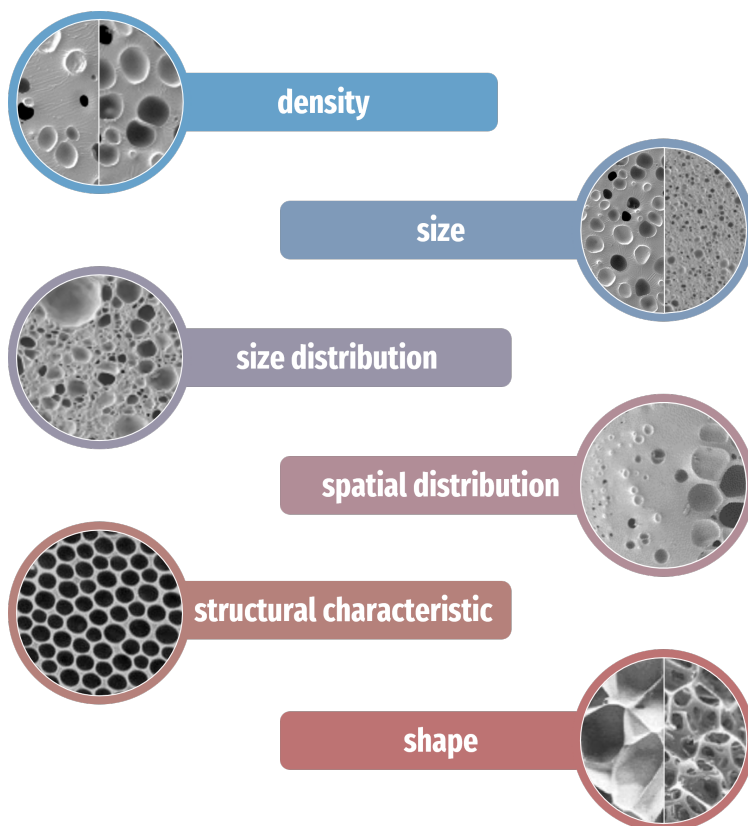


Figure 1.2. Polymeric foam morphology parameters with visual examples. Reproduced with permission [38]. Copyright©2006 The Royal Society of Chemistry. Reproduced with permission [39]. Copyright©2003 Materials Research Society.

fibers or thin films, the conventional foaming strategy is not sufficient. A strategy to produce bubbles in a sample with at least one micro- or nanometric characteristic dimension, involving the use of a gas barrier to prevent gas escape, has been proposed [49, 50]. Li et al. [51] proposed a method to produce a nano-cellular polymer thin film with supercritical CO₂, Siripurapu et al. [52] used a CO₂ impermeable barrier attached to the thin film surface of poly-methyl methacrylate (PMMA), and Orsi et al. [53] created hollow nanoparticles by gas foaming, including the raw particle in a polymer matrix with very low CO₂ diffusivity. Furthermore, The geometric constrain of such samples (i.e. thin films, fibers, nanoparticles) facilitates morphology control by reducing the dimensionality of the system, but further studies have to refine these processes.

1.1.3 Tin based perovskite solar cell

Perovskite materials have gained significant attention in recent years due to their exceptional optoelectronic properties, making them ideal candidates for applications in solar cells [54, 55], light-emitting diodes [56], and other energy-related devices [57, 58]. Organic-inorganic halide perovskite attracted attention due to their ease of manufacture [59], panchromatic absorption of sunlight [54, 60], and long carrier diffusion length [61]. Furthermore, in recent years, perovskite has been used to produce high-performance solar cells with recorded power conversion efficiencies exceeding 20% [62]. Although perovskite solar cells have many benefits, one of the key obstacles to their broader adoption is the use of lead (Pb) in their composition. Pb is a toxic heavy metal that presents serious environmental and health hazards. If not carefully controlled, Pb into photovoltaic systems can seep into the environment, contaminating soil and water, which can harm wildlife and pose risks to human health [63].

The option that has attracted considerable interest is the use of tin-based perovskite materials. Tin (Sn) perovskites are seen as a promising alternative to lead-based perovskites because they have comparable electronic properties and are less toxic [64]. However, the use of Sn perovskites presents significant challenges related to the ease oxidation of tin from its divalent Sn(II) state to tetravalent Sn(IV) and the rapid non-radiative recombination of charge carriers [65]. Oxidation is primarily due to exposure to oxygen and moisture [66, 67], while morphological defects, such as in-

terstitial tin, and lattice misalignment cause carrier recombination [68, 3]. Hence, to achieve high-performance perovskite devices, it is fundamental to passivate and control the morphological properties of the perovskite film [69, 70], namely atomic vacancies and interstitial, lattice misalignment, grain boundaries, pinholes, grain size, and surface defects (Figure 1.3) [71].

1.1.4 Solution processing perovskite thin film

The perovskite films are mainly prepared by solution processing, which allows precise control over the perovskite composition and, potentially, over the microstructure and crystals dimensionality, which is essential for optimizing stability and optoelectronic performances [72]. The process involves spin coating of the precursor dispersion to form a wet thin film, which then evolves into a solid film as the solvent evaporates. Crystal formation is initiated during the spin coating process as the precursor concentration increases, leading to crystal nucleation and growth [73] (Figure 1.4a). Finally, during annealing, the residual solvent evaporates, facilitating further crystal growth and coarsening through Ostwald ripening, leading to a dense and uniform crystals grains layer [74] (Figure 1.4b).

The main challenge in controlling the morphology is the fast and uncontrolled crystallization of the organic-inorganic tin halide perovskite. In fact, the strong Lewis acidity of Sn(II) causes a fast reaction with the organic halides (FAI), thus a fast nucleation of the perovskite crystals, leading to chemical heterogeneity, formation of pinholes, grain boundaries and crystal defects (Figure 1.3), according to the LaMer model [75, 76].

Moreover, several aspects have to be taken into account. In fact, the effect of the complexity of the system, such as the colloidal nature of the system as well as the multiplicity of additives, is not fully understood, and new approaches of non-classical nucleation in combination with classical nucleation theory open a variety of possible nucleation and growth pathways [9, 77] (Figure 1.5).

1.1.5 Strategies for perovskite crystals morphology control

In the past years, several strategies have been employed to control the crystallization dynamic, as well as to avoid the oxidation of the tin based

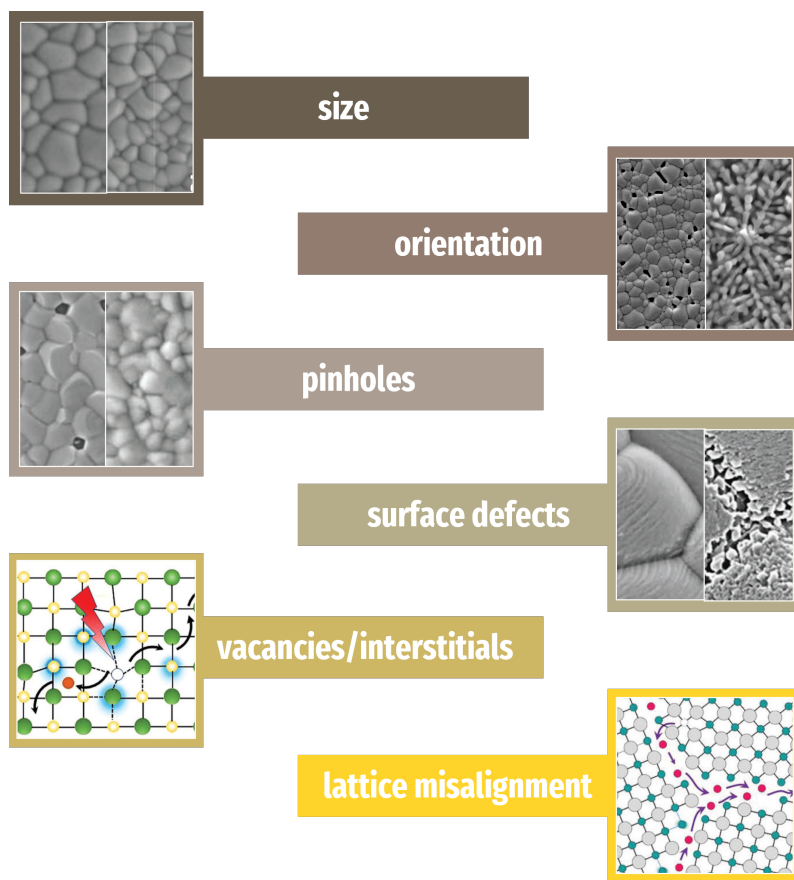


Figure 1.3. Perovskite crystals morphology characteristics with visual examples. Reproduced with permission [71], Copyright©2021 Wiley-VCH GmbH

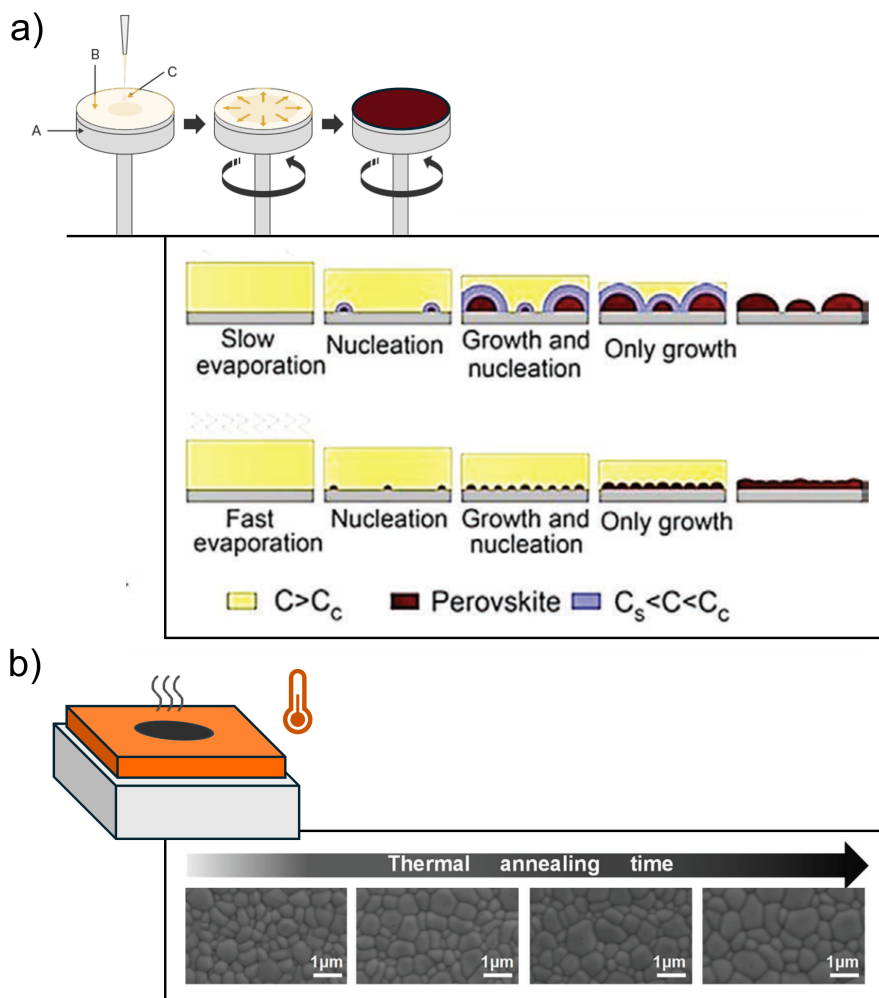


Figure 1.4. Perovskite solution processing scheme. (a) Spin coating of perovskite precursor dispersion during which crystals nucleation and growth occurs, toward the formation of a wet film. Reproduced with permission [73]. Copyright©2021, Wiley-VCH GmbH. (b) Annealing step in which the coarsening of the crystals grains occurs. Reproduced with permission [74]. Copyright©2021 American Chemical Society

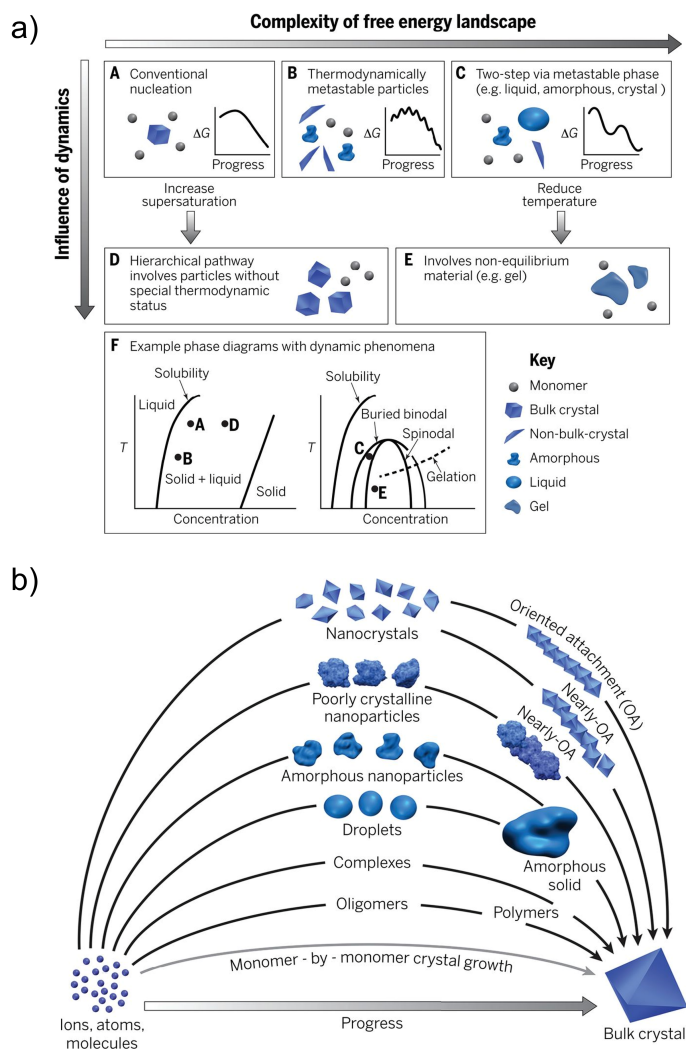


Figure 1.5. Possible nucleation and growth non-classical pathways. Reprinted with permission from AAAS [9].

perovskite, such as, solvent engineering, additive engineering, or process engineering.

The interaction between the solvent and precursor plays a key role in reducing the crystallization rate, as it forms complexes with Sn(II) ions and consequently limits accessibility to the organic halides. For this purpose, polar aprotic organic solvents are used to process the perovskite precursors. These solvents help stabilize the colloidal perovskite nanoparticles [78, 79] and create a stable intermediate phase, effectively slowing down the crystallization kinetic. Firstly, the strategy used for lead-based perovskite was adopted, due to the chemical similarity between Sn(II) and Pb(II), using dimethyl sulfoxide (DMSO) as a solvent for tin-based perovskites. However, there are two main issues in using DMSO to produce tin perovskite thin films. The first is the faster crystallization kinetics of Sn-based perovskite compared to its lead counterpart. This is not related to the different propensity of Sn(II) to react with organic halides, which is weaker, but rather to solvent-solute interactions. In particular, DMSO exhibits weaker coordination with tin ions, leading to accelerated crystallization kinetics [80]. The second issue arises from the solvent-induced oxidation effect of DMSO, which leads to the oxidation of tin to Sn(IV), hence affecting the final properties of the device [81]. In order to use a different solvent system, Di Girolamo et al. [82] provide an exhaustive analysis of solvents, creating a valid playground of alternatives. The use of antisolvents has also been extensively analyzed as it allows external control over the occurrence of nucleation. Their use allows the production of smooth perovskite films with high surface coverage [83, 84] with the absence of pinhole [85].

Considering the additive engineering, an effective strategy was the introduction of nucleation sites using chloride or fluoride additives to reduce the crystallization rate, resulting in a better coverage of the substrate [86, 87]. Other effective additives are those that can form Lewis acid-base adducts, such as π -conjugated Lewis bases [88] and Lewis base polymers [89, 90], or those that can form hydrogen bond interactions [91] which allows for the production of more stable perovskite films, with a reduced amount of pinholes. The use of additives can also affect crystal growth. For instance, the so-called *oriented attachment* has been induced using 2-phenoxyethylamine bromide (POEBR) that template the crystal growth in

a preferred direction, in opposition to the classical monomer-by-monomer addition [92].

The effect of process parameters, such as the temperature of the precursor solution [93] has also been explored, demonstrating the strong effect on the grain size and surface rugosity of the film. Additionally, the use of templates or scaffolds has been tested to drive the growth gaining more uniform crystals grains [94, 95, 96], and to protect the crystal grain from atmospheric oxidation, covering them with a protecting layer [94].

1.2 Aim of the study

The development of novel methods for structuring soft composite film on the micro and nano scale, produced via phase separation processes, is herein proposed. To this purpose, a deeper understanding of the physics and chemistry that govern the morphology build-up during the phase separation is required, together with the implementation of novel processing tool design with a multidisciplinary approach. Two apparently different systems, that can be described by the same classical theory, are analyzed: polymeric porous membranes, and tin based perovskite-polymer composite.

The first part of this study aims to exploit the physical foaming process for the production of polymeric porous membranes with a controlled morphology, namely pore size, shape, spatial distribution, and ordering. The scale-down of the foaming technology to foam a polymeric thin film is required to produce a porous membrane. The micro or nanometric characteristic size of a thin film makes the traditional gas foaming technique unsuitable since the gas, instead of forming bubbles, more easily diffuses out of the sample. Additionally, we explore the impact of the process parameter on the bubble morphology. This investigation aims to assess the influence of a novel category of blowing agents and the application of a pressure treatment to decouple the bubble nucleation from growth steps, providing independent control over bubble density, position, and final radius. Thanks to this technique, an extensive analysis of the physics that govern the physical foaming is addressed, including the coalescence, Ostwald ripening, and shape relaxation stages.

The second part aims to improve the crystallization process as well as

the final device performance of a tin-based perovskite-polymer composite film for optoelectronics. The objective is to examine the impact of a polymeric additive, considering its effect on the different stage of the fabrication process. First, we tested the interactions with the perovskite precursors, than the impact of such an additive on the spin coating process, taking into account the considerable rise in the solution viscosity. Eventually, the device performances are evaluated. The analysis of this system highlights the importance of the nucleation and growth step in the coarsening, paving the way to design a new formulation that exploits the cumulative effect of different molecular weight additives, with the same functional group.

Chapter 2

Liquid foaming of Thermoplastic Polyurethane with Methyal

The present Chapter is based on a manuscript published under the title “Liquid foaming of TPU with Methyal” by L. Miele, E. Di Lorenzo, C. Guissart, E. Di Maio; in *Heliyon*, 2024, Volume 10, Issue 12, e32420; DOI: 10.1016/j.heliyon.2024.e32420

2.1 Introduction

Thermoplastic elastomers (TPE) are currently of great interest in the industry due to their high ductility, resilience, and, most importantly, their environmentally friendly nature [97, 98, 99]. In fact, they are preferred to thermosetting elastomers because they are fully recyclable [100].

Thermoplastic polyurethane (TPU), in particular, are a class of linear segmented block copolymers having hard segments (HS) and soft segments (SS). HS act as multifunctional tie points functioning both as physical crosslinks and reinforcement fillers, while SS form an elastomeric matrix that accounts for the large strain elasticity [99]. The advantage of this peculiar structure is that, by simply varying the SS-HS ratio, the physical properties of the TPU can be tuned [101].

These characteristics make TPU suitable for a wide range of applications, such as supercapacitor, shape memory, automotive parts, and sensor [102], but also for packaging, sportswear, insulation, and construction in the peculiar case of TPU foams. In fact, TPU foams present a series of non-trivial advantages compared to their unfoamed counterparts, including light weight, low thermal conductivity, high strength-to-weight ratio, and dissipation of impact energy, among others [103].

Thermoplastic polymeric foams are traditionally produced with two different techniques: chemical foaming and physical foaming [1]. Chemical foaming relies on a chemical reaction to deliver a blowing agent to the polymer; the reactant can be easily admixed to the polymer during compounding but is often unable to give low-density foams [104, 105, 106]. Physical foaming exploits the introduction of a physical blowing agent (PBA); it requires a special feeding system in the final processing stage, but can push the limit of the specific polymer to the low-density end [20, 21, 107]. As a result of the gaseous physical state of the PBA during the foaming process, physical foaming is also known as gas foaming [1]. Gas foaming is common to different technologies, namely batch [108], extrusion [22], injection molding [23] and steam chest molding [24]. For this study we focus on batch foaming, as it is the simplest process for making foams on the laboratory scale, where small sample sizes, in the order of a few grams, can be utilized. This technique is based on the use of a thermoregulated pressure vessel in which the polymer is placed and the PBA is subsequently injected at a certain pressure to allow sorption into the polymer. After a polymer/gas solution is obtained, phase separation occurs by increasing the temperature or quenching the pressure [1]. This technique is not only very versatile in terms of equipment, but also offers the possibility of a fine control of foaming variables over a wide range, which in turn provides a good control of the final density and cellular morphology of the foam.

The main process parameters are directly suggested by the classical nucleation theory [109] and include the gas concentration before foaming (in batch foaming, it is related to the solubilization pressure, if equilibrium conditions are reached in the sorption process) and the foaming temperature. This set of process variables is completed by the pressure release history $P(t)$, which can dramatically influence the foaming outcome, es-

pecially in terms of the final foam morphology. As a consequence, a comprehensive analysis of $P(t)$ is essential for gaining deeper insights into the complex dynamics governing foam formation and structure development. In the simplest scenario, $P(t)$ is characterized solely by its maximum rate, referred to as the pressure drop rate (PDR).[\[33, 30\]](#).

On top of that, selection of the PBA is pivotal within this process. In fact, the chemophysical properties of the PBA determine its solubility and diffusivity in the polymer, and the volumetric, interfacial and rheological properties of the polymer/gas solution [\[27, 41\]](#). Consequently, the choice of one PBA over the other represents a powerful tool for tuning foam properties, in terms of both foam morphology and foam density.

Possible PBAs for gas foaming include gases like carbon dioxide and nitrogen, in subcritical or supercritical conditions, but also low boiling point liquids, such as pentane, butane, and hydrochlorofluorocarbons [\[49, 103, 110\]](#).

Among these, the use of carbon dioxide as a PBA has gained a lot of interest over the years and has long been established thanks to its properties; in fact, it is not considered a contaminating agent, it does not leave toxic residues in the final product, and it does not cause safety issues. However, the production of low-density foams with CO_2 still remains challenging due to its low solubility and high diffusivity [\[27\]](#).

To overcome these problems, mixtures of CO_2 with other BAs have also been tested. In this case, to achieve the best possible outcome, it is crucial to separately study the role of each PBA during the foaming process with respect to the solubility, foaming kinetics, and setting mechanism, and then design the optimal PBA mixture/recipe [\[111, 27\]](#).

The majority of studies with co-blowing agents deal with the extrusion process. Salerno et al. [\[112\]](#) used mixtures of CO_2 and ethyl lactate (EL) to foam polyesters, while Tsivintzelis et al. [\[113\]](#) and Gendron et al. [\[111\]](#) used mixtures of CO_2 and ethanol for foaming of polycaprolactone (PCL) and polystyrene (PS), respectively. Similarly, in a different work [\[43\]](#), extruded PS foams were prepared by using a mixture of CO_2 and 2-ethyl hexanol, which acted as an efficient additional plasticizer. Reports on the use of CO_2 - H_2O mixtures are also present, like in the works by Zhao et al. [\[114\]](#) and Zhang et al. [\[115\]](#). The blending of CO_2 with an alcohol or a ketone was also proposed for extruded PS sheets of high

compressive strength [116]. In all listed cases, improved foam morphology uniformity and improved foam density were reported. Nevertheless, studies on extrusion foaming cannot be easily transferred to batch foaming. In fact, PDR in extrusion is dictated by the shape of the die and the rheology of the polymer melt regardless of the nature of the PBA. Fewer studies were carried out on batch foaming. The use of CO₂-toluene mixtures [117] and n-pentane (nC5)-CO₂ and cyclopentane(cC5)-CO₂ mixtures [118] on PS was reported [117, 118]. The results suggest that pre-impregnating PS with a blowing agent in its liquid state before the CO₂ batch foaming enhances CO₂ solubility and lowers the glass transition temperature (T_g) of the system, giving higher foam porosity, without modifying the polymer. Similarly, Xiaoqin et al. [119] observed that PP foams blown with a CO₂-n-pentane mixture in batch foaming exhibit a lower foaming temperature, a higher expansion ratio, and a lower cell density relative to those blown with CO₂ alone because of the different gas solubilities of the blowing agents.

As an alternative, the use of low boiling point liquids alone, like pentane and butane, has also been tested, even if no direct comparison with the other mentioned techniques has ever been reported. In the work of Tuladhar and Mackley [120], pentane is impregnated in the polymer melt and then allowed to nucleate and evaporate through a rapid pressure drop to induce phase separation. Effect of foaming parameters such as impregnation time, temperature and sorption pressure on the foaming dynamics of PS and styrene - methyl methacrylate copolymer were studied using pentane as the blowing agent by Salejova and Kosek [121] and Azimi et al. [122, 123]. On the same note, Mostafa et al. [42] studied experimentally and theoretically PS/n-pentane batch foaming. Despite the valuable insights provided by the above mentioned studies, there remains a notable gap in our understanding regarding the criticalities in using a substance in its liquid state as a blowing agent. In this chapter we will address the non-trivial aspects using such a technique, with a special focus on the occurrence of phase transition, from liquid to vapor, and vice versa, that modifies the dynamics of the process.

The possibility of extending the current knowledge about the use of liquid blowing agents in the context of foaming thermoplastic polymers, and TPU in particular, is here faced. Indeed, to the best of our knowledge,

no study reports in detail the technological implications of using a BA in its liquid state, and the pivotal effect of PDR is often neglected.

Several methods have been reported in the literature to prepare TPU foams, including batch foaming [124], and many blowing agents have been used, such as the environmentally friendly CO_2 and N_2 , but also butane, azodicarbonamide and NaHCO_3 [49]. Despite this, the use of liquid blowing agent in TPU foaming is not yet an established practice. In this sense, we remark the work by Hossieny et al. [110], where butane as blowing agent in its liquid state was used to produce microcellular TPU foams. Here, chemical interaction of the liquid with the polymer and consequent redistribution of the hard segments of TPU were exploited through production of crystalline domains that act as nucleating agents.

Dimethoxymethane (Methylal) is a low molecular weight substance with a low boiling point ($42.3\text{ }^\circ\text{C}$) [125]. It is used predominantly as a solvent and as a building block in organic syntheses [126]. It has been used as a blowing agent for thermosetting polyurethane-based foams, alone or in mixtures with 1,1,1,3,3-pentafluoropropane, giving products with non-uniform cellular structures and inadequate thermal insulating performances and compression strengths have been reported [127, 128]. The use of Methylal as the PBA for the production of any thermoplastic polymer foams has never been reported to this day. In the present article, Methylal is used as a PBA in TPU foaming. Because of the thermodynamic properties of the adopted PBA, and its liquid physical state at the temperatures suitable for TPU foaming processing, a proper design of the foaming experiments is at hand. These are detailed and addressed in the study. Preliminary tests are performed on Methylal to study its physical properties under conditions suitable for TPU foaming. Foaming tests with Methylal as sole PBA and as a co-blowing agent with CO_2 and N_2 are performed to demonstrate its potential to adjust the resulting foam features, with the aim of providing improved foaming performance. The possibility of exploiting Methylal to address specific TPU criticalities, such as its stability problems [129, 130], is presented.

2.2 Materials and Methods

2.2.1 Materials

Commercial TPU (Elastollan 45A 12 P, BASF, Ludwigshafen, Germany) was used in the form of pellets, shore hardness 46A, and density 1180 kg/m^3 . Before use, the as received TPU was dried in a vacuum oven at 80°C for 3 h and then stored under vacuum. CO_2 and N_2 (purity 99,99 %) were supplied by SOL S.p.A. (Monza, Italy). Methylal (Dimethoxymethane, $\text{H}_3\text{COCH}_2\text{OCH}_3$, CAS. No. 109-87-5, $M = 76.1$) was supplied by Lambiotte & CIE S.A. (Brussels, Belgium).

2.2.2 Experimental setup

Physical foaming of TPU beads was performed by a custom pressure vessel designed to allow (a) a fine-tuning of the foaming variables (temperature of the expanding matter, pressure and PDR, the latter, especially toward high values), (b) introduction of liquid PBA, (c) fast extraction of the foamed sample, and (d) the possibility of visually inspecting the foaming experiment.

To this end, as illustrated in [Figure 2.1](#), the pressure vessel was equipped with a total of four connections / ports, as described in detail elsewhere [\[25\]](#). A Pt100 temperature sensor (positioned as close to the sample as possible) is installed through the first port to allow temperature control. The second port is connected through a "T" fitting to both a pressure transducer and a manifold for the introduction of the PBA (the manifold is connected to the PBA dosing system and a vacuum pump, necessary for pre-treatment of the beads). The third port is used for the introduction of the beads and is then closed with a $1/2$ " NPT sapphire window (Precision Sapphire Technologies Ltd., Vilnius, Lithuania) to allow visual observation of the experiments. Finally, the fourth port connects to a ball valve (10–80 NFH ball valve, High Pressure Equipment Company, Erie, USA), activated by an electromechanical actuator, and allows fast and reproducible release of the PBA. This port is also used to extract the samples rapidly, as the foamed TPU beads are small enough to be dragged by fluid flow to the exit [\[25\]](#). A total of five TPU beads is tested simultaneously in the internal compartment of the vessel to ensure the distribution of the data acquired

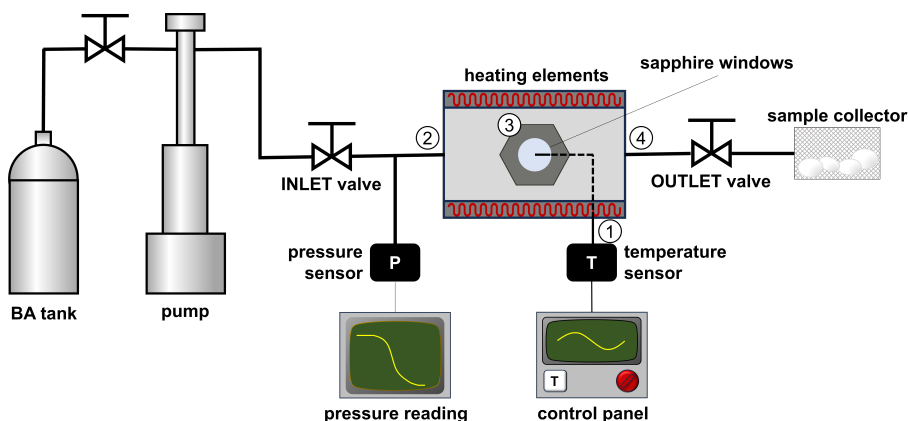


Figure 2.1. Schematic of the experimental setup used for the liquid and gas foaming experiments where: (1) indicates the port connected to the thermocouple; (2) indicates the port connected to the pressure sensor and the manifold; (3) indicates the viewing port, with a sapphire window, and (4) indicates the port used for the release of the PBA and concomitant expulsion of the samples.

from each experiment. The setup thus described works with gaseous and liquid blowing agents: when using a gaseous blowing agent (CO_2 and N_2 , namely), the second port is connected to the gas dosing system, while when using a liquid blowing agent (Methylal, namely), it is connected to a high pressure syringe pump (model 500D, Teledyne ISCO Syringe Pumps, Thousand Oaks, USA) that is capable of dosing the liquid inside the vessel at the desired pressure. The liquid is loaded in the syringe pump through a tube inserted directly into the Methylal bottle, while the piston of the pump is retracted to suck the liquid.

2.2.3 Liquid and gas foaming experiments

Foaming experiments were conducted in three ways, namely (i) liquid-vapor foaming, (ii) liquid foaming and (iii) gas foaming, depending on the physical state of the PBA and desired foaming conditions.

The procedures is: (i) The liquid-vapor foaming technique requires a PBA under vapor-liquid equilibrium conditions at foaming temperatures. In this case, the foaming pressure is the vapor pressure. The pre-treated

TPU beads are inserted into the vessel and kept under vacuum at 80 °C for 1 h to remove the humidity absorbed by the granules during handling. The liquid blowing agent (Methylal) is then injected into the vessel at ambient pressure with a pipette through port two. After pressure-tight closing the vessel, the desired temperature is imposed. At the given temperature, thermodynamic equilibrium and the vapor pressure are reached if any liquid is present. After a solubilization time of 30 minutes, foaming is performed through a quick pressure drop at a controlled PDR. Here, the solubilization pressure corresponds with the vapor pressure. As a consequence, it is regulated through the choice of the temperature and decoupling of these two process parameters is not possible. For this same reason, this method allows only for low-pressure foaming, as the temperatures suitable for TPU foaming correspond to equilibrium vapor pressures lower than 10 bar (see sections [subsection 2.2.5](#) and [2.3.1](#)). (ii) In the liquid foaming technique, pressures are higher than the vapor pressure and the PBA is in the liquid state. The pre-treated TPU beads are inserted in the vessel and kept under vacuum at 80 °C for 1 h to remove humidity absorbed by granules during handling. The liquid blowing agent is then injected into the vessel with a syringe pump that is capable of imposing a desired pressure. After a solubilization time of 30 minutes, foaming is performed through a quick pressure drop at a controlled PDR. With this method, pressures up to 90 bar were reached. (iii) The gas foaming technique requires a gaseous PBA. In this case, TPU pellet pre-treatment was the same as described in the previous case, but the pressure of the gaseous BA, namely CO₂ and N₂, is here regulated with a carbon dioxide pump (Nex10 Liquid Carbon Dioxide Pump, Supercritical Fluid Technologies INC., Newark, US) directly connected to the relative gas tank. The solubilization time was 1 hour instead of 30 minutes depending on the different diffusivities of the gases with respect to liquid Methylal. This same technique is also used to perform experiments with mixtures of liquid and gaseous blowing agents (CO₂ and Methylal mixture as well as N₂ and Methylal mixture). The preparation of the mixture is ensured by preliminary placing the pre-treated beads in a Methylal bath for at least 1 hour before being inserted into the vessel.

2.2.4 Pressure drop rate measurement

An important control variable of the physical foaming method through pressure quench is PDR [131]. The characteristic time of the pressure drop is very short ($\tau_{PD} \sim 1000\text{ms}$), thus a very high data acquisition rate is required. For this reason we measured the PDR through a PLC (SIMATIC S7-1200 CPU, Siemens, Munich, Germany) with a sampling rate $\tau_m \sim 1\text{ms}$. This device registers the pressure values over time and provides as output a curve $P(t)$. The shape of this curve depends on test conditions and PBA nature. We used numerical methods to analyze the $P(t)$ curve and calculate the largest time derivative (PDR). First, we applied a moving average to smooth out the short-term fluctuations and highlight the longer term trend. The average involves 99 data points corresponding to a time interval (10 ms) that is two orders of magnitude smaller than the characteristic time of the pressure reduction (1000 ms). Then we applied the midpoint method to evaluate the derivative. This derivative operation amplifies the noise of the signal, thus a moving average (99 points) was again applied to smooth out the data. At the end of the processing, PDR was evaluated as the highest peak value of the $-dP/dt$ curve. A visual representation of this evaluation is shown in Figure 2.2. This method proved to be the most efficient among all the tested ones for PDR evaluation (namely, line interpolation and curve fitting). The main advantage lies in the independence from a mathematical model to describe the $P(t)$ curve and from the human bias (on the interval in which the curve is interpolated). Also, amongst the advantages it stood out that we could apply this method to any $P(t)$ curve, even when non trivial shapes were detected.

2.2.5 Liquid-vapour equilibrium Methylal

The vapor pressure of Methylal was investigated in order to avail data useful for foaming tests [132, 133]. The experiments were conducted in the above-mentioned mini-batch vessel, which acts as a closed system. For the scope, this was equipped with a valve for the injection of Methylal in its liquid state. We used the following procedure. First, we filled the mini-batch with Methylal in its liquid state at ambient temperature. Then we increased the temperature to a predefined value (that is, 96, 118, 135 and

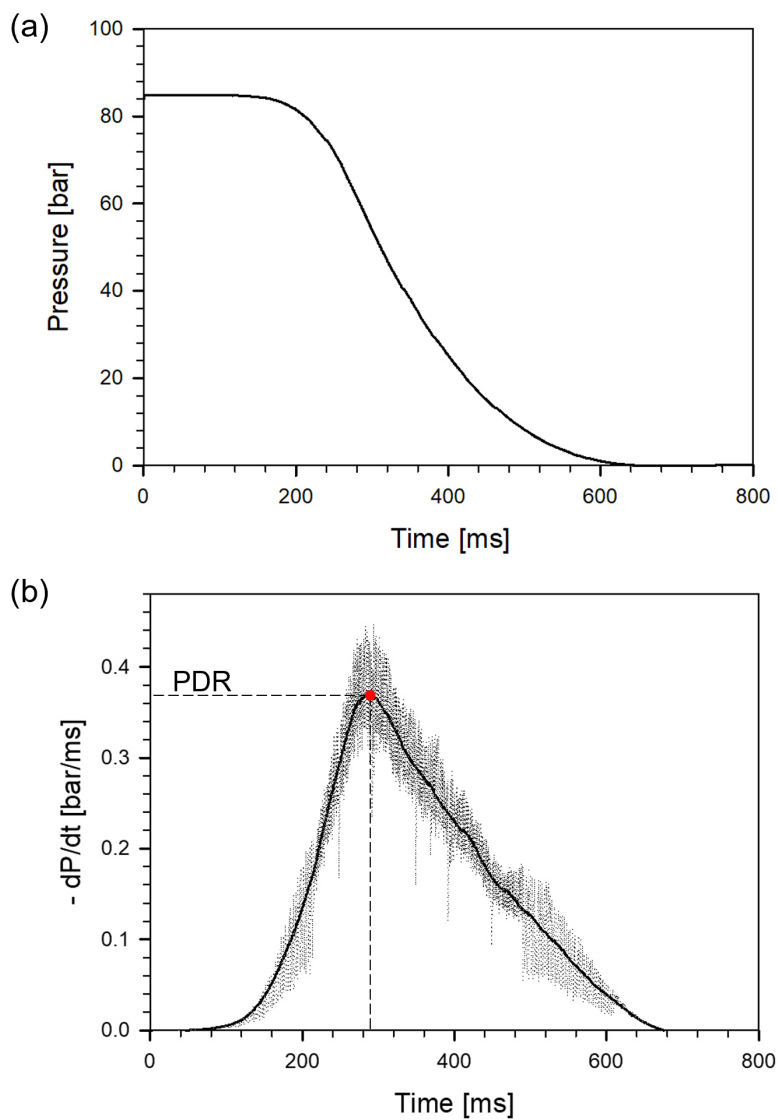


Figure 2.2. (a) Pressure reduction over time; (b) moving average of central derivative of $P(t)$ (black) and central derivative of $P(t)$ (gray).

154 °C) and we waited until the gas-liquid equilibrium was reached, that is, when the temperature and pressure of the system remained stable for at least 1 hour, with an error of 5%. The pressure value at each condition was recorded as the vapor pressure of Methylal at that specific temperature value. For all measurements, the temperature sensor happened to be submerged in the liquid. Equilibrium parameters value thus found were used as temperature-pressure conditions to perform liquid-vapor foaming experiments with Methylal. It is important to note that, before experiments, the cell was evacuated with a vacuum pump, while during the experiments, the sapphire window was used to check the presence of liquid inside the vessel.

2.2.6 TPU foam characterization

Density measurements, optical microscopy, and scanning electron microscopy were used to characterize the TPU samples after foaming. The density measurements were performed using a density kit mounted on a laboratory balance (MS104S/01, Mettler Toledo, Columbus, Ohio). The test standard used was ASTM D792-00: by measuring the weight of the foamed sample both in air (w_{air}) and in water (w_{water}), density of the sample is calculated as:

$$\rho = \frac{w_{air}}{w_{air} - w_{water}} \times \rho_{water} \quad (2.1)$$

For each sample, the density was calculated as the mean of five replicates. Every measurements was made immediately after foaming. Days after foaming, as also seen elsewhere [134, 129], shrinkage of the beads was observed, but this will not be explored in detail in the present chapter. An optical microscope (Stemi 508, Zeiss, Oberkochen, Germany) was used to observe the morphology of TPU foams obtained with the liquid foaming technique, while a scanning electron microscope (SEM Merlin VP, Zeiss, Oberkochen, Germany) was used to observe the morphology of the TPU foams obtained with the gas foaming technique, because they had a much finer morphology. To prepare the optical microscopy and SEM specimen, TPU foams were cut using an ultrathin stainless steel blade. In the case of SEM specimens, the cross section was then coated with a thin layer of

gold using a sputter coater (Auto Sputter Coater, Agar Scientific, Essex, UK). In the case of SEM, a ten days delay between the foaming experiment and the characterization caused shrinkage to occur before the images were collected. Again, this aspect will not be discussed in detail in the present chapter. Weight measurements of TPU beads were also performed before and after foaming to collect additional information.

2.2.7 Solubility and swelling measurements

Information about the interaction of Methylal with TPU in terms of solubility and consequent swelling of the beads was collected by measuring the weight and volume of the beads before and after immersion in a Methylal bath. Weight measurements were performed with a Mettler Toledo laboratory balance and then used to evaluate solubility in terms of weight fraction, x_e , at equilibrium:

$$x_e = \frac{w_{beads}|_{t=\infty} - w_{beads}|_{t=0}}{w_{beads}|_{t=0}} \quad (2.2)$$

Where $w_{Methylal}|_{t=\infty}$ is the weight of the Methylal absorbed inside the beads after the immersion process and $w_{beads}|_{t=0}$ is the weight of the beads before the immersion process. Volume measurements were made by taking pictures of the beads at the times of interest and then analyzing them with ImageJ [135]. In each image, the "edge detection" and "profile integration" commands were used to detect the edges of the beads and subsequently derive the beads volume values. From these data, swelling, Sw , was evaluated as:

$$Sw = \frac{V|_{t=\infty} - V|_{t=0}}{V|_{t=0}} \quad (2.3)$$

Where $V|_{t=0}$ and $V|_{t=\infty}$ are the volume before and after immersion in Methylal.

2.3 Results and discussion

First, we will explore the thermodynamic properties of Methylal, the interaction of Methylal with TPU, specifically in terms of solubility and

swelling, and the peculiar shape of the pressure drop history noticed while performing the foaming experiments. Then, we will thoroughly describe the results of the foaming experiments, for each of the three ways described in [subsection 2.2.3](#): (i) liquid-vapor and (ii) liquid foaming experiments with Methylal alone and (iii) gas-foaming experiments with CO₂ and Methylal as co-blowing agents. In each case, effect of process parameters and foam morphology will be presented. The results of foaming experiments with N₂ alone and N₂ and Methylal as co-blowing agents will not be presented because, in the same conditions used for CO₂, no foaming was detected.

2.3.1 Liquid-vapor equilibrium Methylal

The experimental results of the investigation of the thermodynamic properties of Methylal are shown in [Figure 2.3](#). In the range mentioned above, the vapor pressure varies from 4.41 to 15.4 bar, consistent with data from the literature [[132](#), [133](#)]. We can see that the maximum pressure at which we can use Methylal at equilibrium is approximately 9 bar, as imposed by the maximum temperature at which the polymer can be processed (polymer melting temperature). As a consequence, the use of Methylal at higher pressures is possible only in the fully liquid state.

2.3.2 Solubility and Swelling

To test the interaction between Methylal and TPU, solubility measurements were performed. This preliminary study is fundamental to our research because it allows us to understand Methylal potential as a PBA (high solubility is required for any substance to be considered a good PBA). Under ambient conditions, $x_e = 0.493$, and at 5.5 bar and 116.6 °C $x_e = 0.744$. These values are high enough to demonstrate that Methylal has the potential to be a good PBA. In fact they are orders of magnitude higher than the typical solubility values of gaseous blowing agents (namely N₂ and CO₂) in TPU [[41](#)]. Methylal also shows a strong swelling ability in its liquid state, with $Sw = 69.8\%$ at 45 bar and 131.8 °C. Here, the high amount of swelling is related to the high solubility of Methylal in TPU. Finally, the weight of the samples before and after foaming were recorded and an 11.5% w/w weight loss after contact with Methylal was observed.

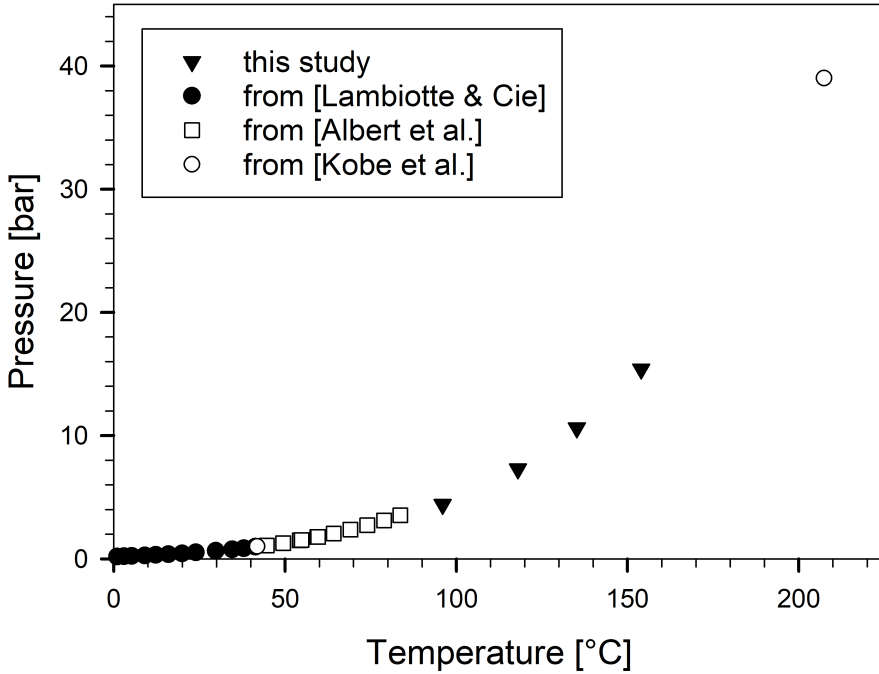


Figure 2.3. Vapor pressures of Methylal. Data represented with the full circles are taken from [125], data represented with the hollow squares are taken from [132] and data represented with the hollow circles are taken from [133].

In fact, it is possible that Methylal extracts low molecular weight fractions or additives from the granules. This hypothesis was corroborated by the in-situ observation of the liquid foaming experiments, at the end of which some material, itself foamed during the pressure release, could be seen on the surface of the sapphire window, as shown in Figure 2.4. The image does not represent a clear evidence of this phenomenon, and specific analytical experiments are required to quantify the molecular mass and the nature of the extracted material. Nevertheless, it is evident that at the end of the foaming experiment the sapphire window loses transparency, as a consequence of the presence of traces of material.

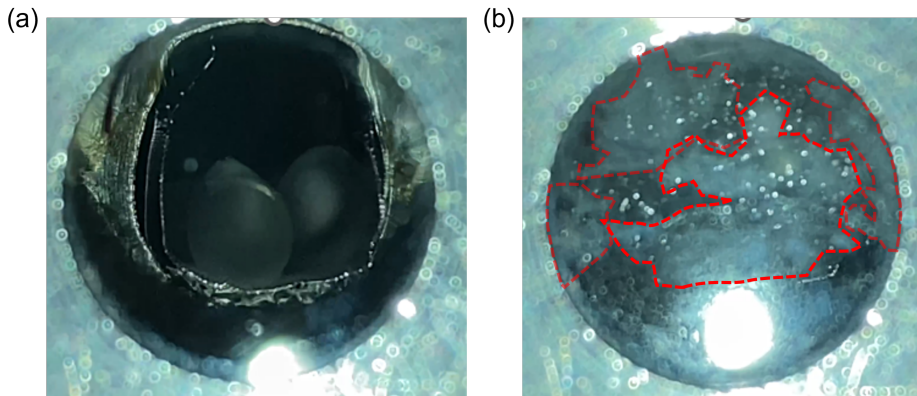


Figure 2.4. Pictures of the sapphire window taken before (a) and after (b) foaming. Traces of material are visible on the glass surface in figure (b) as marked by the red dashed outline.

2.3.3 Pressure drop history

PDR is of key importance in foaming because it influences the thermodynamic thrust that causes phase separation. We observed a different behavior with different PBA as reported in [Figure 2.5a](#): for typical gaseous blowing agents such as CO_2 , we observed a one-step reduction in pressure. For the liquid blowing agent (i.e., Methylal), we observed a two-step reduction in pressure: a fast reduction of pressure, much faster than the one-step reduction registered with CO_2 , followed by a slower one. We infer that the faster PDR observed for the liquid case is due to the negligible compressibility: with valve opening, the volume available to the liquid increases causing an immediate pressure drop, only partially sustained by the liquid to vapor transition.

To support this thesis, in [Figure 2.5b](#) - we report the different pressure reduction curves of different experiments carried out at the same temperature of $132.0\text{ }^\circ\text{C}$ and at different solubilization pressures, namely 30, 45 and 60 bar. It is interesting to note that, regardless of the set pressure, the pressure at which the slope changes is almost the same in all cases and is approximately 12 bar, which is in the vicinity of the vapor pressure of Methylal at the test temperature ($p = 10.96\text{ bar}$, $T = 135^\circ\text{C}$). Furthermore, the second slope remains the same for all experiments, with a value

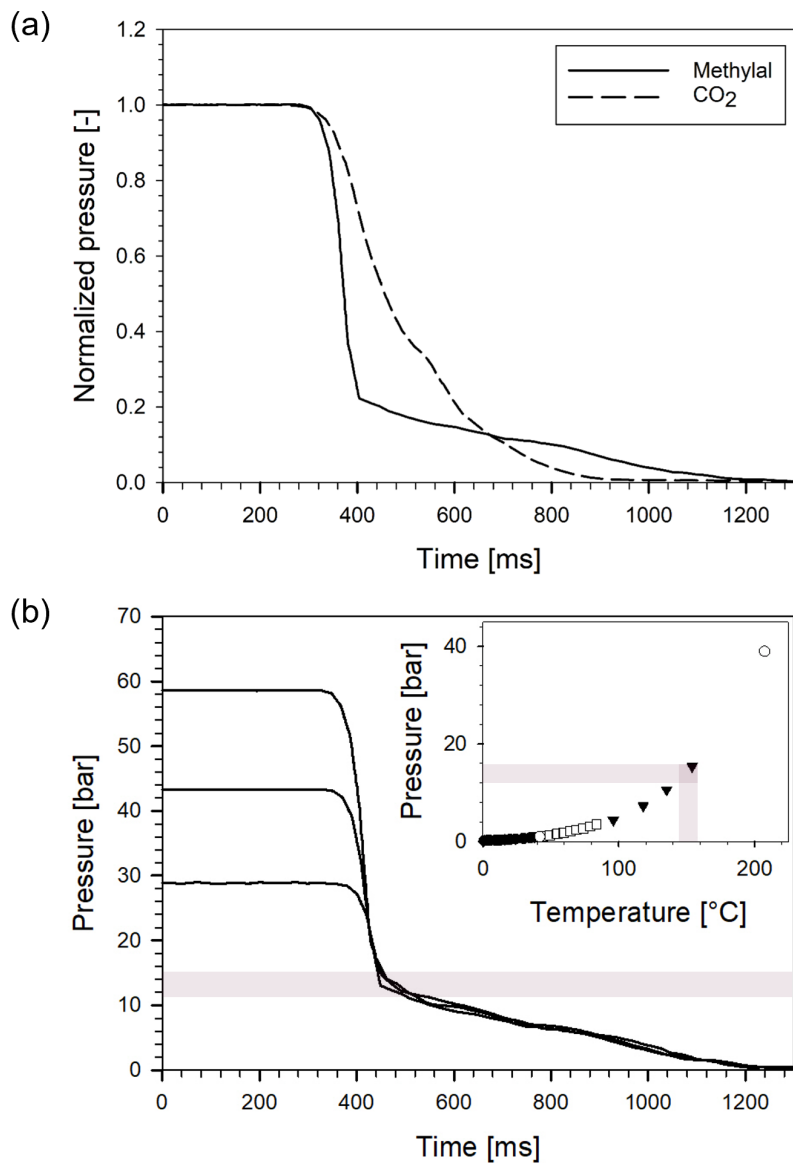


Figure 2.5. (a) Pressure (normalized by the solubilization pressures) reduction curves of foaming experiment with gaseous blowing agent (dashed line) and liquid blowing agent (solid line) and (b) pressure reduction curves of liquid foaming experiments alone at different values of solubilization pressure.

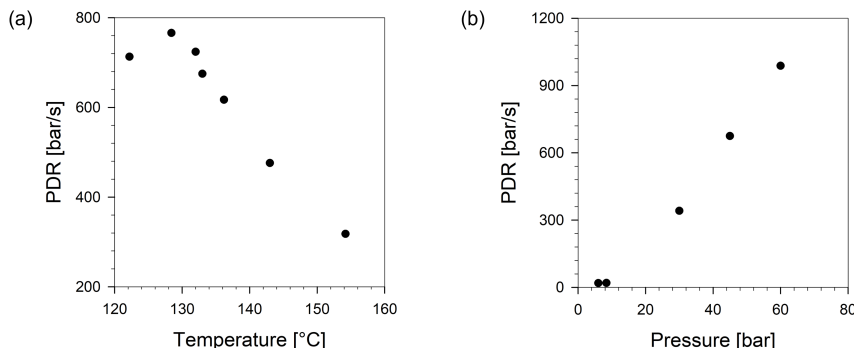


Figure 2.6. PDR measurements: (a) effect of foaming temperature, solubilization pressure = 45 bar; (b) effect of pressure, foaming temperature = 132 °C.

of 0.44 bar/s. The advantages of a structured pressure drop was demonstrated in several works, however, this is usually difficult to obtain because it requires complex control systems [136, 137]. On the other hand, we were able to obtain a double slope pressure drop by just exploiting the phase transition of the blowing agent, which is of great potential in foaming.

2.3.4 Liquid-vapor foaming

This technique does not allow high pressures to be reached and the pellets do not foam until at least 6.5 bar are reached. Since the solubility is high enough under ambient conditions to provide formation of gas bubbles, the failure of these foaming attempts is probably due to low PDR (less than 18.7 bar/s). Moreover, since the system only works at equilibrium, temperature and pressure are always coupled, and it is more difficult to study the effects of all parameters separately. No data will be reported on these foams due to negligible attained density reduction.

2.3.5 Liquid foaming

The effect of process parameters on the outcomes of liquid foaming experiments are here presented. Parameters of interest in this study were

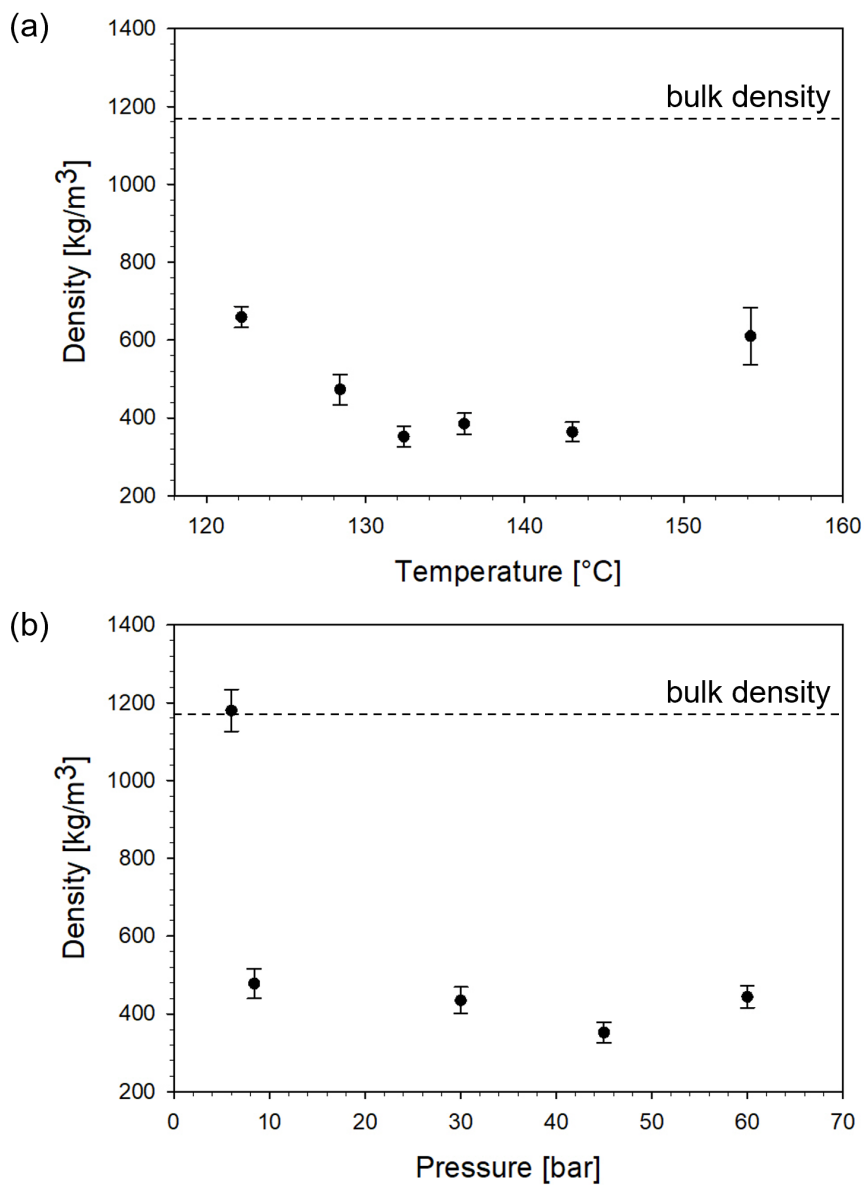


Figure 2.7. Effect of temperature (a) and pressure (b) on the mean density of TPU foamed by the liquid foaming technique.

temperature, gas concentration (here, equivalently, solubilization pressure, as we designed the foaming process to achieve uniform gas concentration), and PDR. The results are given in terms of the density and morphology of the final product. First, we examined the effect of temperature at a fixed pressure of 45 bar, and a variable PDR (Figure 2.6a). As it can be seen in Figure 2.7a, the density decreases as the temperature increases until, at approximately 135.0 °C, a minimum of 352 kg/m³ is reached, which is slightly larger than the one produced with a similar technology by Hossieny et al. [110]. Above 135 °C, the viscosity reduction induces the foam collapse, resulting in the rise of the density [1]. The available foaming temperature window at 45 bar is between 123.4 °C and 143.0 °C. Then, we studied the effect of pressure at a fixed temperature of approximately 132.0 °C and at a variable PDR, depending on the maximum pressure value (Figure 2.6b). The results are shown in Figure 2.7b. We can see that, at pressures lower than 6.0 bar and PDRs lower than 18.7 bar/s, foaming does not occur, confirming the results obtained with the first approach to the liquid foaming method (see subsection 2.3.4). At higher pressures, the density is noticeably reduced, reaching values comparable to those obtained in the temperature sweep experiments. This can also be connected to the fact that a higher PDR can be reached at higher foaming pressures, which would confirm the importance of the PDR in inducing foaming. The morphology of the foamed samples under the different foaming conditions is shown in Figure 2.8 and Figure 2.9.

As it is visible, the TPU beads (five, in a typical experiment, see section 2.2.2) weld together at foaming in these experimental conditions. Regardless of the low quality of the images, the influence of the process parameters is clear and consistent with the density measurements. When the pressure is lower than 6 bar and the PDR is lower than 18.7 bar/s, foaming does not occur, while, at higher PDR, foaming begins to occur (Figure 2.9d-e-f). The foamed product shows a very coarse morphology with a large fraction of large bubbles and a small fraction of smaller bubbles. As pressure increases, the bubbles seem to get smaller in dimension. Indeed, the color of the foam fades towards white as a hint to the reduction of the bubble diameter. It is worth noticing that in all cases (full temperature and pressure ranges) the bubble and samples shape is not well defined. This is probably due to the high solubility of Methylal in TPU and conse-

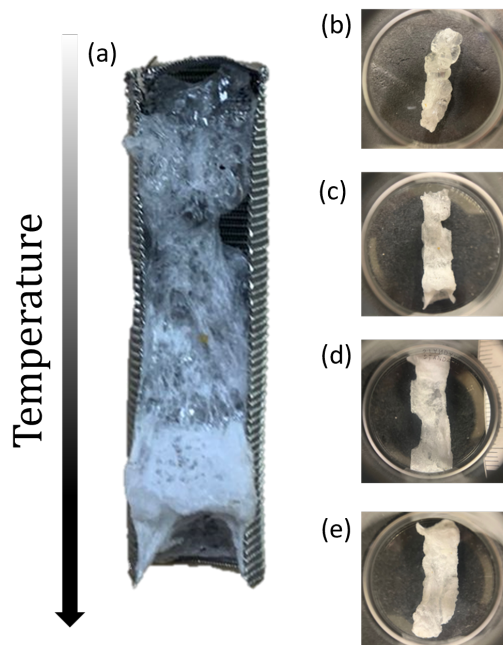


Figure 2.8. Morphology of the foamed TPU beads at constant pressure ($p = 45$ bar) and with varying temperature: (b) 122.2 °C, (c) 128.4 °C, (d) 132 °C and (e) 136.2 °C. Picture (a) is a larger-magnification copy of picture (c) and shows a sample with a varying morphology from top to bottom. This has been related to a minor varying temperature inside the vessel.

quent high expansion followed by extreme bubble coalescence and collapse of the entire foam. This peculiar behavior can be addressed to the effects of Methylal on TPU, described in [subsection 2.2.7](#). Indeed, the very high solubility and subsequent swelling are linked to an increase in the mobility of the HS chains in TPU, which is in turn responsible for an increased foaming ability [110]. When excessive, this increase in chain mobility, and subsequent decrease in viscosity, will facilitate the bubble coalescence and collapse [29, 138]. To avoid this problem, the gas foaming technique with Methylal as the co-blowing agent was performed, as fully described in [Section 2.3.6](#).

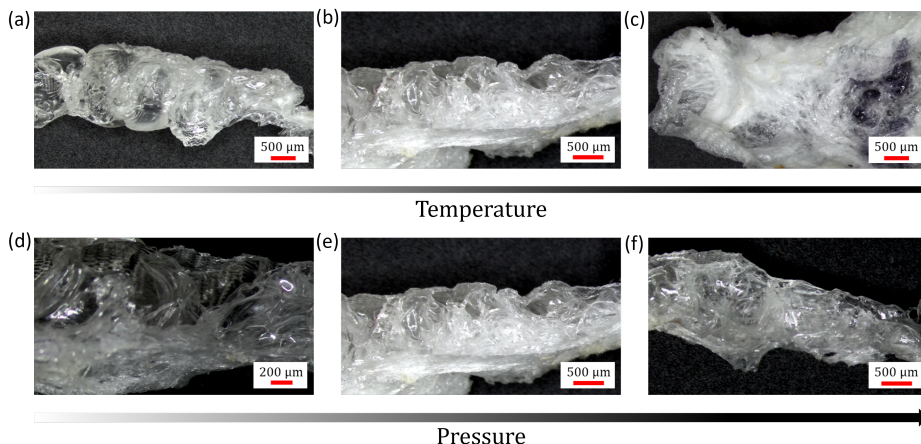


Figure 2.9. Morphology of the foamed beads at the end of the liquid foaming experiments performed at constant pressure $p = 45$ bar and temperature (a) $T = 120$ °C, (b) $T = 136$ °C and (c) $T = 150$ °C. Morphology of the foamed beads at the end of the liquid foaming experiments performed at constant temperature $T = 133$ °C and pressure (d) $p = 30$ bar, (e) $p = 45$ bar and (f) $p = 60$ bar.

2.3.6 Gas foaming with Methylal as a co-blowing agent

Gas foaming experiments with Methylal as a co-blowing agent were performed to reduce the amount of Methylal within the TPU beads and thus prevent the collapsed morphology typical of liquid foaming experiments. CO_2 was used as gaseous BA in a mixture with liquid Methylal. All experiments were carried out under the same temperature and PDR conditions ($T = 80$ °C and $\text{PDR} = 500$ bar/s), while pressure was changed from 40 to 120 bar to understand its effect on the final foamed product. The final foamed products were very different from those obtained with the liquid foaming technique. Indeed, beads welding does not occur; on the contrary, they stay separated and they also show a noticeably increase in volume. The effect of pressure on the final foamed products in terms of the resulting density is shown in [Figure 2.10](#) (blue symbols). As we can see, as the pressure increases, the density of the foam decreases.

The same study was carried out with Methylal and CO_2 alone as BAs

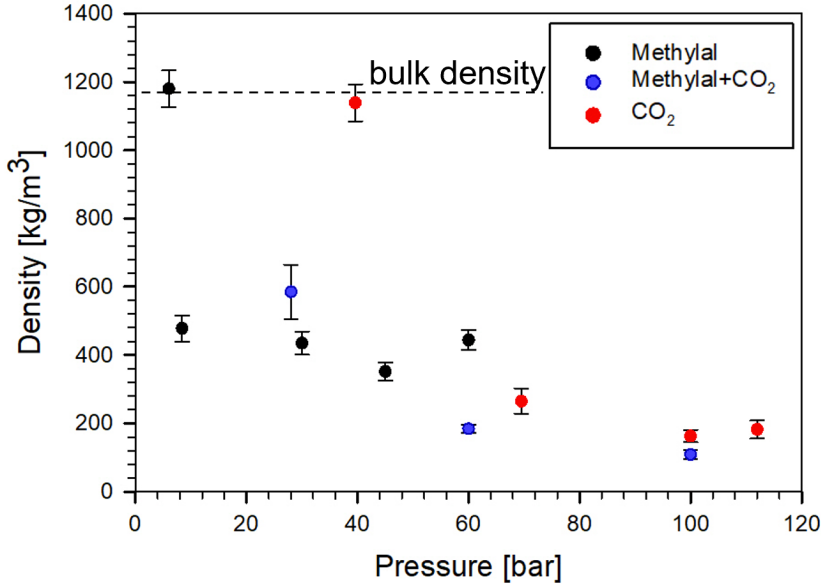


Figure 2.10. Density of foamed TPU beads at different values of foaming pressures and with different blowing agents: Methylal (black circles), Methylal + CO₂ (red circles) and CO₂ (green triangles).

and the results are compared in Figure 2.10 (black and red symbols, respectively). The minimum density value reached with CO₂ alone is 163 kg/m^3 , which is in agreement with the CO₂ blown TPU foams reported by Jun et al. [139]. It is visible that the technique that uses CO₂ and Methylal as co-blowing agents is superior to gas foaming with CO₂ alone and liquid foaming with Methylal alone. In fact, this technique ensures the lowest final densities at almost every pressure value, with a minimum density of 110 kg/m^3 , so a reduction of almost 40% compared to samples foamed with CO₂ alone. Furthermore, when using the mixture, the process parameters window is broadened, allowing foaming at lower pressures, as in the case of Methylal alone. The lowest densities are obtained with the CO₂/Methylal mixture and prove that adding Methylal induces an increase of BA availability with respect to CO₂ alone. The morphology of the beads foamed with the CO₂/Methylal mixture was studied and is shown in Figure 2.11.

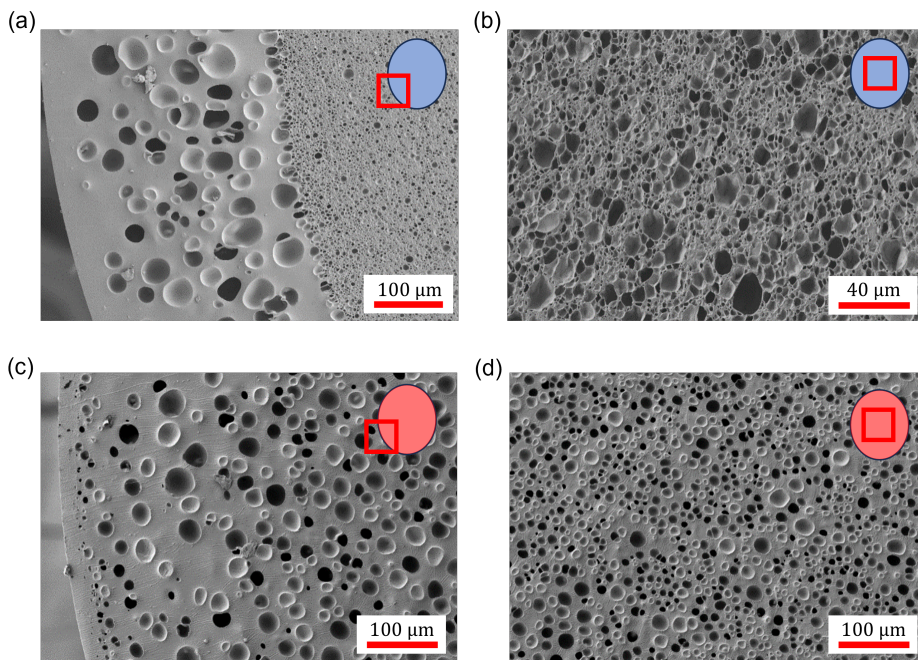


Figure 2.11. Morphology of TPU beads after the gas foaming experiment with the CO₂/Methylal mixture (a,b) and with CO₂ alone (c,d) as the PBA. Pictures are taken at the center of the foamed beads (b,d) and on the boundary (a,c).

This morphology appears to be significantly different from the morphology of the beads foamed with the liquid foaming technique (Figure 2.9). The bubbles are smaller in dimension. Moreover, the bubble walls are well defined, and neither buckling, nor collapse occur. In general, this technique significantly improves foam morphology compared to the liquid foaming technique. The presence of a large boundary region is detected in which the bubbles appear larger in dimension and less dense (Figure 2.11a). This probably occurs because of the partial escape of Methylal during CO₂ sorption [46]. Comparison with the morphology of CO₂-only foamed TPU beads confirms this hypothesis (Figure 2.11b). Further studies on Methylal diffusivity in TPU could improve our understanding of dense skin formation [140]. When CO₂ is the sole PBA, the bubbles are larger in dimension

and less dense, with a more defined bubble wall, just as they appear in the boundary region of [Figure 2.11c-d](#).

2.4 Conclusions

Methylal proved to be an excellent physical blowing agent for TPU. It has a very high solubility in the polymer of interest and thus causes a large swelling of the polymer pellets due to an enhancement in chain mobility. Additionally, a strong plasticizing effect and a low molecular weight fraction extraction from TPU were detected. When used alone, in its liquid state, a non trivial pressure drop reduction is detected, caused by the occurrence of phase transition. This proves that a complex pressure reduction can be obtained by simply exploiting the nature of the BA rather than using a regulation system. However, the resulting foamed samples display moderate densities (i.e., 400 kg/m^3) with collapsed morphologies, probably due to the extremely high Methylal solubility and swelling ability. When used in combination with other gaseous blowing agents, namely CO_2 , improved results are obtained. The densities of the foamed samples are lower than those reached with the liquid foaming technique (110 kg/m^3 vs. the above mentioned 400 kg/m^3), and the morphologies do not show collapse. As seen from the SEM images, bubbles are smaller in dimension and a boundary region is detected. The results achieved with the combination of the two blowing agents are also better than those obtained with gaseous blowing agents alone, namely CO_2 , both in terms of final density and foaming window, which means that Methylal highly enhances the foaming ability of CO_2 and could be of help in industrial practices. Overall, Methylal is applicable in foaming technologies, but further studies would enhance the understanding of its role as a blowing agent.

Chapter 3

Bubble dynamic manipulation in polymeric foaming

The present Chapter is based on a manuscript published under the title “Bubble dynamic manipulation in polymeric foaming” by L. Miele, A. Abate, K. Taki, E. Di Maio; in *Soft Matter*, 2024, 20(44), 8845-8854; DOI: 10.1039/D4SM01040J.

3.1 Introduction

Bubbles are ubiquitous in everyday life and industry, for example when embedded in liquid [141] or solid matrices [142] to form foams. The bubble formation and evolution process, with the stages of bubble nucleation, growth, and stabilization, is central to optimizing processes and performance. Specifically, bubble growth is a complex phenomenon in which mass, momentum, and energy are transported in a two-phase, two-component system comprising many bubbles within a viscoelastic fluid [143, 144]. In modeling approaches, simplified approximations are necessary to reduce the complexity of the problem and address the lack of experimental data for specific polymer/blowing agent systems [1].

From an experimental point of view, monitoring bubble formation and evolution is required to validate the models. Specifically, concerning polymer foaming, numerous custom apparatus for the visualization of bubbles

have been developed [145, 146, 147, 26]. These systems were designed to enable the study of different foaming stages, including bubble nucleation in both homogeneous and heterogeneous cases [148, 29, 149], bubble growth [30, 150], and eventually, setting or coalescence [29]. Furthermore, they have been used to validate various processes, such as the core back operation of injection moulding [151]. While the proposed techniques offer significant consistency and flexibility, there are some drawbacks. With regard to the study of bubble growth, the time interval during which bubble analysis can be performed is limited due to the interaction and overlapping of bubbles in the image. In 2003, Acierno and Grizzuti [152] introduced the so called "inverse quenching" technique to study rheological properties of a semi-crystalline polymer at a given degree of crystallization. The technique exploits the effect of temperature on the dynamics of crystallization to regulate degree of crystallinity of the polymer. By lowering the temperature, on a molten polymer, they initiate the crystallization, and by subsequently raising the temperature, they preserve the crystalline phase in a quenched state and gain the opportunity of long-term study. The presenter technique somehow resembles and was inspired by the "inverse quenching" technique using pressure rather than temperature, to quench bubbles, rather than crystals. In particular, the presented technique will exploit the effect of pressure over the bubble dynamics, leveraging the compressibility of the gas within the bubbles and the ability to inflate or deflate the same. This allows us to control and decouple bubble nucleation, growth, and collapse, hence controlling the bubble dynamics. We will show how this simple idea discloses a wealth of important outcomes, together with the abundance of collectable data.

3.2 Materials and Methods

3.2.1 Materials

Isotactic homopolypropylene granules (PP, F-300SP, Prime Polymer Japan, melting temperature of 165 °C) were compression molded at 230 °C and 10.0 MPa for 10 min, then slowly cooled to ambient temperature to achieve slab thickness of 0.5 mm. Eventually, 5mm diameter disks were formed by punching. Nitrogen with purity >99.999 % was used as a

physical blowing agent.

3.2.2 Visual observation apparatus

The bubbles dynamics manipulation experiments were performed using a custom-made visual observation apparatus. The apparatus consists of a high-pressure autoclave with sapphire windows and automatic valves to finely control the pressure of the gas, as described elsewhere [153]. The PP disk was sandwiched between the sapphire windows, and a 0.5 mm thick C-shaped spacer fixes the distance between the windows. A camera (EMVC-CB130C3, MISUMI, Japan) with a long-distance microscope (VH-Z50L, KEYENCE, Japan) was used to capture the bubble evolution. The autoclave pressure (P) is controlled by two solenoid valves (SSPD-8, Keihin, Japan) connected to a programmable logic controller (PLC, KV-Nano, Keyence, Japan) that operated the valves at a response time of 10 ms. In addition, needle valves were used to adjust the gas flows. In a typical test, after the sample is loaded, the autoclave is purged with nitrogen and heated to the set temperature ($T = 180\text{ }^{\circ}\text{C}$), which is kept constant for the duration of the experiment. When the test temperature is reached, P is brought to and held constant for 60 min at saturation pressure, P_{sat} , (in the range 6.5-8.5 MPa), to form a polymer/gas solution in equilibrium with the external gas phase. Starting from equilibrium conditions, a general pressure treatment is shown in Figure [Figure 3.1](#). Here, after saturation, the pressure treatment starts with a pressure quench to nucleate bubbles, from P_{sat} to the nucleation pressure, P_{nucl} (details are reported in [subsection 3.3.1](#)). After a certain time, t_{nucl} , the pressure is slightly increased to P_{inverse} , in order to control the bubble growth stage, in fact, decoupling the growth from the nucleation stage. The pressure is maintained constant for a sufficient period of time, designated as t_{growth} , during which various bubble dynamics can be observed and modeled (details are reported in [subsubsection 3.3.2](#)). Eventually, to tailor the bubble morphology, in some experiments pressure is periodically changed in a range from P_{down} to P_{up} , n_{cycle} times, with a period t_i (details are reported in [subsection 3.3.3](#)).

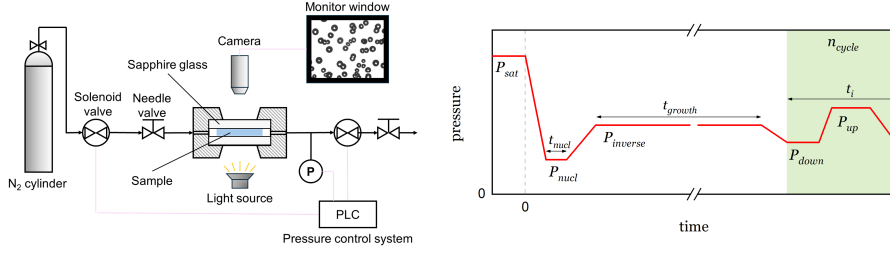


Figure 3.1. Visual observation apparatus scheme, with the pressure vessel and the details of the sample between two sapphire windows, the light source at the bottom and the camera above (left); general pressure treatment (right).

3.2.3 Image analysis

Using ImageJ (FIJI) software [154], the images were binarized, then the "fill holes" and "watershed" functions were used to erase the light reflection inside the bubbles and to separate the overlapped bubbles, respectively. The bubble properties were then quantified using the "analyze particle" tool (considering bubbles as particles). The resulting details of the bubbles are: the area (A), the major radius (R_{max}) and the minor radius (R_{min}) - the primary and secondary semi-axis of the best-fitting ellipse, their average (the bubble radius, R), the coordinates of the center of mass of each bubble (X_{Mi}, Y_{Mi}), the distance between two bubbles (d), and the roundness (RND), defined as:

$$RND = \frac{4A}{\pi R_{max}^2}. \quad (3.1)$$

As we are interested in studying each and every bubble separately, all the data collected in the previous operation were analyzed with a custom-made MATLAB script to track the bubbles, thus measuring the time evolution of the details listed above.

3.3 Results and Discussion

3.3.1 Bubble number density

We use the pressure quench technique to induce bubble nucleation. From P_{sat} , P is rapidly reduced to the nucleation pressure, P_{nucl} . As extensively reported in the literature, the driving force for bubble nucleation is the associated gain in the volumetric Gibbs energy[1], ΔG . According to the classical nucleation theory [155], in the simple case of homogeneous nucleation,

$$\Delta G = \frac{16\pi\gamma^3}{3(P_{sat} - P(t))^2}, \quad (3.2)$$

where γ is the interfacial tension and $P_{sat} - P(t)$ is the pressure reduction. Given ΔG , the number of stable nuclei that form per unit volume and time, the nucleation rate, $J(t)$, reads [156]

$$J(t) = C_0 f_0 \exp\left(\frac{-\Delta G}{k_b T}\right) = C_0 f_0 \exp\left(\frac{-16\pi\gamma^3}{k_b T 3(P_{sat} - P(t))^2}\right), \quad (3.3)$$

where C_0 is the concentration of gas within the polymer matrix, f_0 is a frequency factor for gas molecules that describes the rate at which the nuclei with critical radius are transformed into stable bubbles [157], k_b is the Boltzmann constant, and T is the temperature. By integrating the nucleation rate over time, we obtain the total number density of bubbles, N_{total} , which can be expressed as a function of the pressure reduction, as proposed by Goel and Beckman [156]:

$$N_{total} = \int_{t_0}^t J(t) dt = \int_{P_{sat}}^{P_{nucl}} J(t) \frac{dP}{(dP/dt)}. \quad (3.4)$$

N_{total} can be measured (at least, estimated), for example, by looking at the cross section of a foam, and Eq. 3.4 can be experimentally validated. For example, several authors have reported an exponential increase of N_{total} with an increase of P_{sat} , when quenching to ambient pressure and the other processing variables are kept constant [156, 147, 30]. Herein, to vary N_{total} , we modulate P_{nucl} at constant P_{sat} , instead of changing P_{sat} .

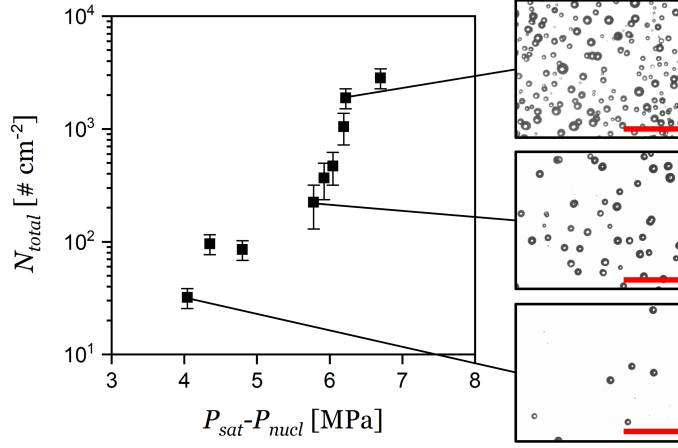


Figure 3.2. Bubble number density vs. pressure reduction at a fixed $P_{sat} = 8.1$ MPa. Scale bar is $1000 \mu m$.

Specifically, for the sake of clarity, P_{nucl} varies from ambient pressure to any higher pressure. Figure 3.2 reports the effect of the pressure reduction ($P_{sat} - P_{nucl}$) on N_{total} at fixed $P_{sat} = 8.0$ MPa, $T = 180$ °C and pressure drop rate of 500 MPa/s. As expected in view of Eqs. 3.2-3.4, the adjustment of P_{nucl} in the present chapter proves to be an effective tool to control bubble nucleation and allows us to design the pressure treatment required to achieve the desired bubble morphology, as described in the following sections.

3.3.2 Bubble growth manipulation

Following nucleation, the evolution of bubbles is driven by the pressure difference between the bubble pressure (P_{bub}) and P , as well as interfacial and viscoelastic forces. The multitude of nucleated bubbles, with a variety of sizes, relative distances, shape, and gas concentration profiles, creates a rich landscape of behaviors and phenomena that can be simultaneously observed and studied. For example, Figure 3.3 provides a (partial) glimpse of the observable phenomena. In particular, we observed various growth regimes of isolated bubbles (a), Ostwald ripening (b), bubble coalescence

(c), and bubble interaction causing shape changes (d). As reported in previous works which made use of visual observation apparatus [26, 29, 150], the extent of bubble growth eventually (quite rapidly) leads to interactions and overlap among bubbles, in fact terminating the visual observation experiment. To avoid such a scenario and maintain a long-lasting bubble playground, it is sufficient to reduce bubble growth. As described in detail in the next section, increasing the pressure may serve this purpose.

Inverse pressure quench treatment

The inverse pressure quench treatment consists in a pressure increase (from P_{nucl} to $P_{inverse}$, with $P_{nucl} < P_{inverse} < P_{sat}$) after the first pressure reduction responsible for the nucleation stage, with the objective of reducing the bubble growth by exploiting the compression of the gas in the bubble and the mass transport of gas from the polymer/gas solution to the bubble or vice versa. The latter depends on the gas concentration profile around the bubble and the boundary condition at the bubble radius dictated by P_{bub} and at the outer disk surface dictated by P [30]. Figure 3.4 shows an example of an inverse pressure quench treatment with its effect on the kinematics of R over time. We can identify three growth dynamics corresponding to the pressure variation: (I) first bubble growth following pressure quench (with a lag time for the first bubble observation); (II) pressure increase and corresponding bubble size reduction; (III) second bubble growth at rather constant pressure. Following the appearance of a bubble, a concentration gradient is formed in the polymeric matrix that maintains the gas flow to the bubble [144]. With the increase in pressure from P_{nucl} to $P_{inverse}$, the bubble volume reduces, and a new boundary condition is established that defines a non-trivial gas concentration profile, enriching the possible evolution scenario.

In Figure 3.5 we can compare the effect of the inverse pressure quench treatment ($P_{sat} = 8.0$ MPa, $P_{nucl} = 2.8$ MPa and $P_{inverse} = 4.2$ MPa - red curve and red-framed image in Figure 3.5) with two pressure quench treatments (without the inverse pressure quench): one quenching from $P_{sat} = 8.0$ MPa to $P_{nucl} \approx 0$ MPa (black curve and black-framed image in Figure 3.5) and one quenching from $P_{sat} = 8.0$ MPa to $P_{nucl} = 4.2$ MPa (blue curve and blue-framed image in Figure 3.5). For each pressure treatment, the bubble images at $t = 20$ s are reported. It is quite evident that the

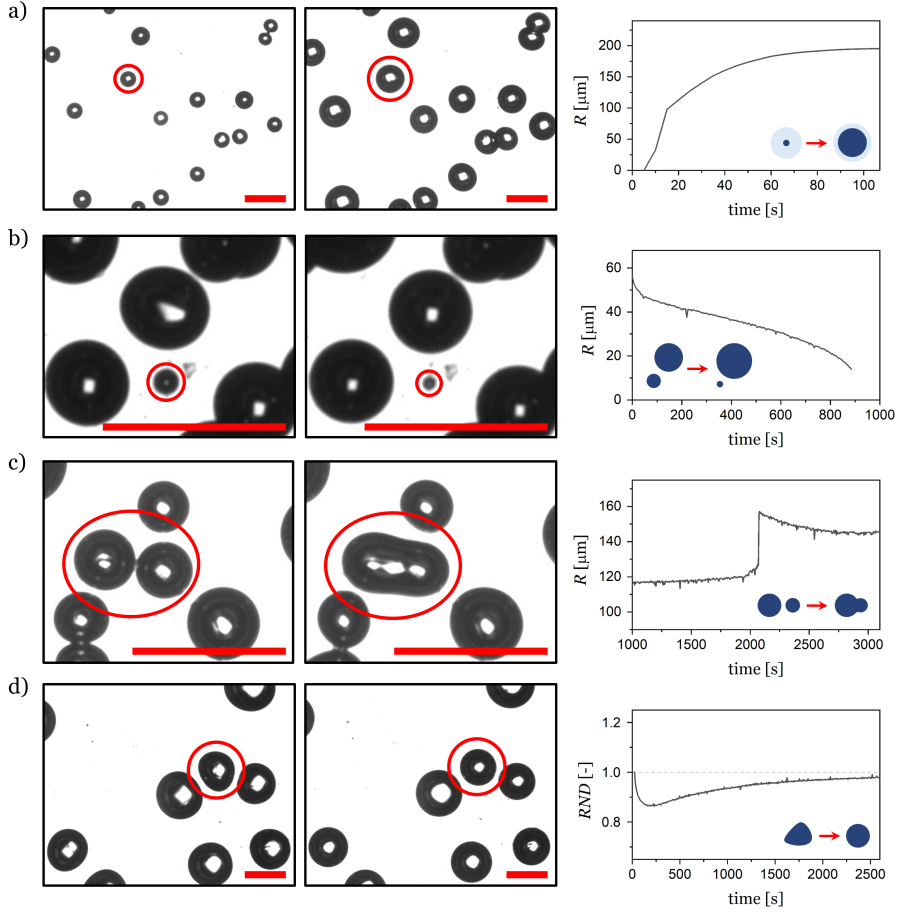


Figure 3.3. Bubble images reporting four different phenomena, namely, (a) diffusion driven bubble growth; (b) bubble dissolution caused by Ostwald ripening; (c) bubble coalescence; (d) bubble shape variation as a consequence of bubble impingement. For each phenomenon the left images report two subsequent frames separated by an arbitrary time interval. On the right, the representative parameter evolution. Scale bar 500 μm .

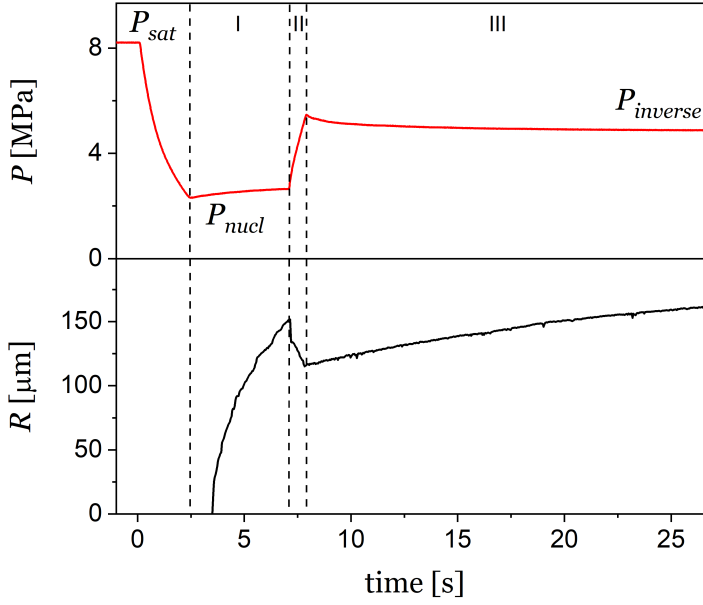


Figure 3.4. Inverse pressure quenching treatment: imposed pressure history (red) and bubble radius evolution (black); three different growth dynamics regimes corresponding to the pressure variation can be identified: first bubble growth (I), size reduction caused by the pressure increase (II), second bubble growth (III).

large pressure drop from 8.0 to 2.8 MPa (black) is responsible for the nucleation of a large number of bubbles and their rapid overlap due to growth, impeding long-term growth study. Reduction of pressure quench from 8.0 to 4.2 MPa (blue) induces the nucleation of a small number of bubbles, too small to get a wide perspective of the different growing behavior and coupled phenomena. Instead, the pressure quench treatment allows the formation of a large number of bubbles (comparable to the case of the 8.0 to 2.8 MPa drop - black) but the subsequent pressure increase impedes the bubbles overlapping and allows long-term growth monitoring. The value of inverse pressure quench treatment emerges with the use of two additional examples (Figure 3.6). In a first example, to study a system with virtu-

ally all isolated bubbles, we can induce the nucleation of a small number density of bubbles (see [subsection 3.3.1](#)) and then use the inverse pressure quenching treatment to keep them small so that the average inter-bubble distance is larger than the bubble radius ([Figure 3.6a](#)). [Figure 3.6b](#) reports the temporal evolution of R for 3000 s. To the best of our knowledge, this is the first reported experiment in which bubble growth in polymeric foaming is observed for so long, allowing for a thorough study of the growth phenomena.

In a second example, to study a system with interacting bubbles, we can induce the nucleation of a larger number density of bubbles, and then use the inverse pressure quenching treatment to prevent bubbles overlapping in the image. In this case, a long-lasting bubble observation ([Figure 3.6c](#)), allows the study of the mechanical interaction (leading to impingement, shape variation, Ostwald ripening or coalescence, as will be detailed in the following ([Figure 3.6d](#)).

While in the first example ([Figure 3.6a,b](#)), the undisturbed growth of bubbles with a relatively narrow size distribution can be monitored for hours, in the second example ([Figure 3.6c,d](#)), the wealth of different observable phenomena is evident: coalescence (underlined by the presence of peaks in the curves, as in [Figure 3.3c](#)), Ostwald ripening (underlined by the presence of monotonically decreasing curves - as in [Figure 3.3b](#)), as well as growth and shape change, all concurrently occur.

In fact, the inverse pressure quench technique proves to be an effective tool for decoupling nucleation from growth, for regulating the average value of R , and for preventing bubbles from overlapping. This allows us to study growth and to interrogate and validate the growth, impingement, ripening, and coalescence models. Finally, we foresee the use of such an experimental platform for the characterization of the properties of the polymer/gas system relevant to foaming and to derive constitutive models.

Focus on bubble growth

The bubble growth phenomenon consists in the bubble volume variation over time. The driving force for growth is the difference $P_{bub} - P$ [30]. As mentioned in [subsubsection 3.3.2](#), a change in P causes the gas in the bubble to expand (or shrink, depending on the sign of the pressure change) against the inertial, the Laplace, and the viscoelastic forces exerted by the

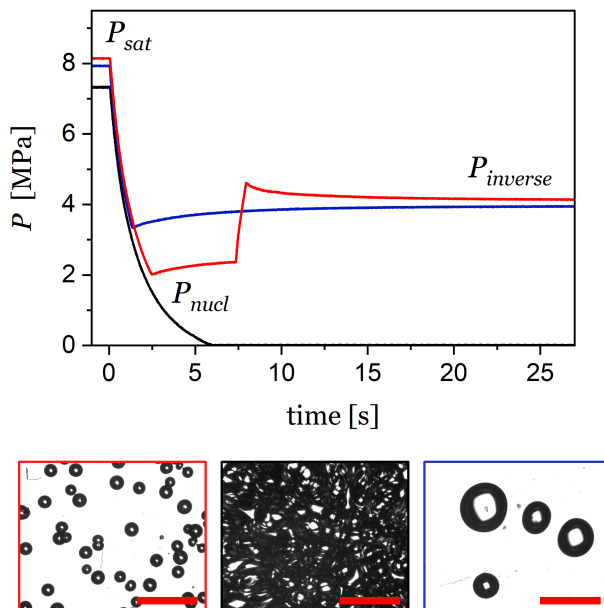


Figure 3.5. Pressure history of the inverse pressure quench treatment (red) and comparison with two simple pressure quench treatments (black and blue) and images of the sample at a $t = 20$ s. Scale bar is $1000 \mu m$.

surrounding polymer/gas solution. Furthermore, mass transport of the gas solubilized in the surrounding polymer/gas solution is involved in equilibration of the resulting changes in the boundary conditions at the bubble surface and the disk surface.

Several models have been proposed in the literature to describe the dynamics of bubble growth in the case of isolated as well as of multiple bubbles [158, 30, 145, 31, 32, 159]. In order to support our experimental evidence and help the discussion, it is worth describing a simplified model that fits our case. The experimentally observed characteristic growth time is $\mathcal{O}(10^2 \text{ s})$, while the relaxation time of the polymer is $\mathcal{O}(10^0 \text{ s})$ (see Appendix A). We may hence neglect the elastic contribution of the polymer response to deformation. The characteristic strain rate can be experi-

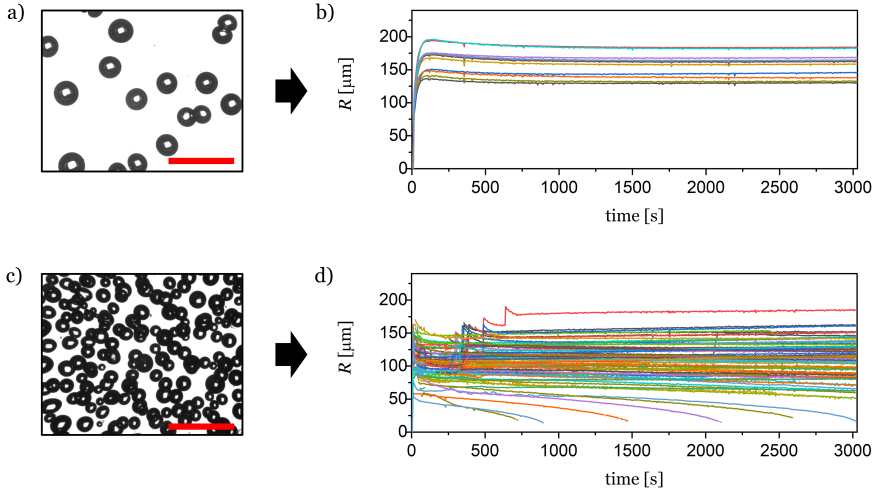


Figure 3.6. Inverse pressure quenching treatment outcomes. (a) Image of the sample after 25 s from inverse pressure quench ($P_{sat} = 8.1$ MPa, $P_{nucl} = 2.3$ MPa, $P_{inverse} = 4.8$ MPa) for isolated bubbles system. (b) Corresponding bubble radius evolution for all of the bubbles appearing in the image. (c) image of the sample after 25 s from inverse pressure quench ($P_{sat} = 7.3$ MPa, $P_{nucl} = 1.8$ MPa, $P_{inverse} = 2.3$ MPa) for interacting bubbles system. (d) Corresponding bubble radius evolution for all of the bubbles appearing in the image. Scale bar is $1000 \mu\text{m}$.

mentally evaluated as $\dot{R}/R = \mathcal{O}(10^{-2} \text{ s}^{-1})$ and, based on the flow curve reported in the Appendix A, we can assume Newtonian behavior, with viscosity $\eta = 10^4 \text{ Pa s}$. Finally, inertial forces $F_i = 4\pi\rho R^2 \dot{R}^2$ are negligible with respect to the others. From the momentum balance, in a spherical coordinate system with the origin in the center of the bubble, the one-dimensional ordinary differential equation describing the evolution of R reads:

$$\frac{dR(t)}{dt} = \frac{R(t)}{4\eta} \left(P_{bub} - P(t) - \frac{2\gamma}{R(t)} \right). \quad (3.5)$$

Where P_{bub} can be evaluated considering the mass transfer at the bubble interface derived from the mass balance:

$$\frac{d}{dt} \left(\frac{4\pi R^3 P_{bub}}{3 R_g T} \right) = 4\pi R^2 D \left. \frac{\partial c}{\partial r} \right|_{r=R}. \quad (3.6)$$

Where R_g is the gas constant, c is the gas concentration and D is the diffusivity of the gas with respect to the polymer. The gas concentration profile is evaluated, according to the Fick's law, as follows:

$$\frac{\partial c}{\partial t} = D \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) \right]. \quad (3.7)$$

This model assumes the initial bubble radius (R_0) as the hypothetical radius of a stable nucleus [30, 159, 28]. The experimental validation of this assumption is not trivial, as is the measurement of the radius of a gas nucleus. After applying the inverse pressure quench treatment, we are able to stabilize the growing bubble radius over time by keeping the system at constant pressure $P_{inverse}$ (Figure 3.6a-b). Starting from this point, we can manipulate the bubble dynamics by modulating P . In this way, we can study the growth dynamics decoupled from the nucleation.

An example is shown in Figure 3.7, in which the effect of the modulation of P on the bubble dynamics is reported. The graph reports the value of R over time for a bubble $R_0 \approx 160 \text{ }\mu\text{m}$, previously stabilized using the inverse pressure quench technique (see Paragraph *Inverse pressure quench treatment*). By decreasing the pressure from $P_{inverse}$ to P_{down} , R increases accordingly. After P reaches the set value, the bubble growth proceeds. Furthermore, increasing the pressure from P_{down} to P_{up} , R decreases, fol-

lowing similar, although mirrored dynamics.

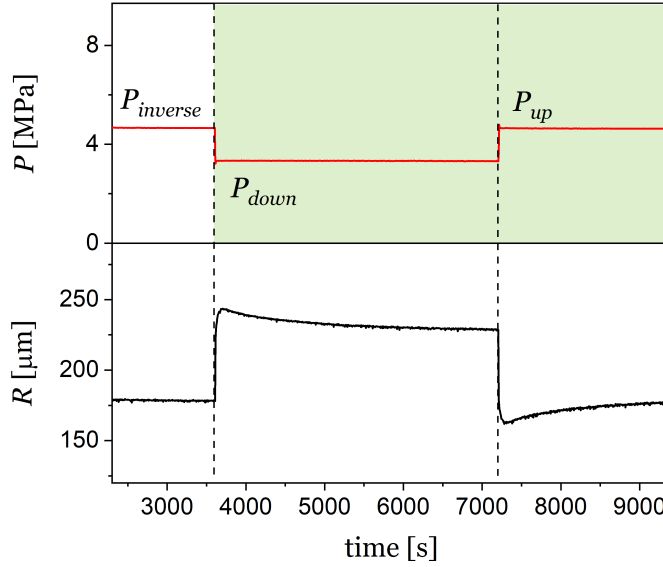


Figure 3.7. Effect of bubble pressure on bubble growth dynamics. Imposed pressure history (red) and bubble radius evolution (black). The bubble inflate or deflate when the pressure is reduced or increased.

The observation of bubble growth dynamics over a long period unveils a rather unexpected behavior. After the pressure variation, R evolves towards a stable value in a non-monotonic way, going through a maximum or minimum value depending on the pressure change sign (negative or positive, respectively). More studies are required to investigate this phenomenon, not excluding the effects of multiple-bubble interaction. Finally, the possibility of manipulating the growth rate and thus the deformation rate of the polymer/gas solution surrounding the bubbles is considered with the aim of exploiting the treatment for measuring the physical properties of the polymer/gas solution involved in the growth dynamics, listed in Eqs. 3.5-3.7, as proposed in the work of Garbin and colleagues [143, 160]. For example, Figure 3.8 shows the effect of the pressure variation rate on the bubble growth dynamics, for treatments where the pressure is reduced at

various rates, from 0.002 MPa s^{-1} to 5.0 MPa s^{-1} . Here, R is normalized with the plateau value of R long after the pressure variation (R_{st}). Specific studies devoted to the implementation of the proposed treatment for the characterization of the polymer/gas solution are required, which is outside the experimental and theoretic scope of this study.

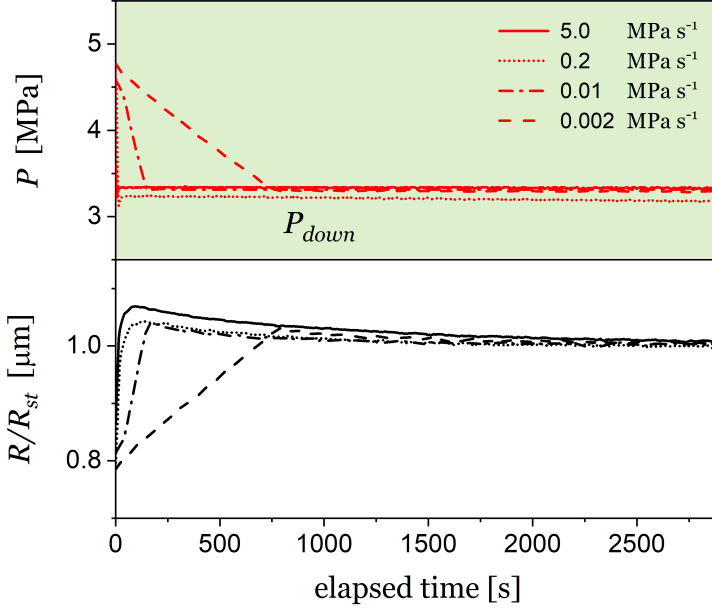


Figure 3.8. Effect of pressure variation velocity on bubble growth dynamics. Imposed pressure history (red) and bubble radius evolution (black).

Focus on Ostwald ripening

Ostwald ripening is the phenomenon in which a small particle dissolves at the expense of the growth of larger surrounding particles [161]. The driving force is the concentration gradient that arises as a result of the difference in surface curvatures. In the case of gas bubbles, the pressure inside the bubble changes with the curvature (Laplace's law), resulting in a

proportional change in gas concentrations at the bubble interface (Henry's law). This local change in the gas concentration causes the gas to diffuse through the polymer/gas solution from the smaller bubble toward the larger ones, eventually inducing the dissolution of the former. As a final result, Ostwald ripening causes the bubble size distribution to coarsen over time. The mathematical description of Ostwald ripening was first proposed by Lifshitz and Slyozov [162] and independently by Wagner [12], today referred to as the LSW theory [11], and used mainly to describe solid particle systems[5]. With respect to gas bubbles, Lemlich et al. [163] modeled the coarsening of bubbles in gas-liquid foams, while Von Neumann proposed a law to describe the coarsening of 2D foams [164, 165]. Finally, Glazier and Weaire [166] published an extensive review of the scaling laws that govern the coarsening of liquid foams induced by ripening of the smaller bubbles. In these works, the coarsening is expressed as the mean radius evolution of a large group of bubbles, and no detailed description of the evolution of each single bubble is considered.

On the other hand, the effect of Ostwald ripening can be analyzed by observing the evolution of each single bubble within the system, as shown in Figure 3.6d. The curves with a negative slope are related to dissolving bubbles, which eventually disappear. A quantitative analysis of the dissolution of smaller bubbles can be performed based on the data reported in Figure 3.9, which shows the evolution of R over time for the small, dissolving bubbles. Epstein and Plesset [167] derived an analytical expression for the diffusion-controlled dissolution of a single isolated air bubble in water, considering the effect of interfacial tension on the internal pressure of the bubble. The model has been later validated both on water-based systems [168, 169] and on molten polymer-based systems [170] and describes the evolution of R as follows:

$$R(t)^3 - R_0^3 + A(R(t)^2 - R_0^2) = Bt, \quad (3.8)$$

where A and B are defined as:

$$A = \frac{2M_w\gamma}{\rho_g R_g T}, \quad (3.9)$$

$$B = -\frac{6Dk_H M_w \gamma}{\rho_g}. \quad (3.10)$$

In Eqs. 3.9 and 3.10, ρ_g is the density of the gas, M_w is the molar mass of the polymeric matrix, and k_H is Henry's constant. A and B can be evaluated by fitting the experimental data and the averaged results of the fitting procedure are reported in Table 3.1 along with values predicted using literature data for the parameter in Eqs. 3.9 and 3.10 ($\rho_g = 10^1 kg\ m^{-3}$, $M_w = 10^2\ kg\ mol^{-1}$, $T = 180^\circ C$, $\gamma = 10^{-2}\ N\ m^{-1}$, $D = 10^{-9}\ m^2 s^{-1}$, $k_H = 10^{-4}\ mol\ N^{-1}\ m^{-1}$) [171, 172, 59]. While A shows a good agreement with the predicted value, we note a large discrepancy for B , probably indicating a delay in the observed dissolution dynamics with respect to predictions. To further analyse the problem, we examine the dissolution time, t_d , which can be derived by the Epstein-Plesset model [168] as follows:

$$t_d = \frac{R_0^2}{3Dk_H} \left(\frac{R_0\rho_g}{2M_w\gamma} + \frac{1}{R_gT} \right). \quad (3.11)$$

Using data from the literature, $t_d \approx 10^1\ s$, which is much smaller than the experimental value ($\mathcal{O}(10^3\ s)$). This delay in the dissolution time has been reported in the literature, in particular with reference to multiple bubble systems, and is attributed to the so-called *diffusive shielding*, by which a bubble dissolves slower than an equivalent isolated one, due to the increase in local gas concentration caused by dissolution of neighboring bubbles [173, 174]. The interplay between Ostwald ripening and diffusive shielding can lead to delayed dissolution or even stabilize a bubble to an equilibrium radius, as reported by Weijs et al. [175]. The use of a more complex model with respect to the isolated bubble model is in order and is left for future work. Here, we demonstrate the use of the proposed treatment as a novel experimental platform to study the dynamics of bubble dissolution and, more generally, the physics of bubble interaction.

Table 3.1. Fitting parameters of the Epstein and Plesset model [167] for our experiments at $T = 180\ ^\circ C$ and $P = 4.0\ MPa$ and by using literature data for variables in Eqs. 3.9 and 3.10.

parameter	fitting value	predicted
A	$67 \pm 7.5\ \mu m$	$53\ \mu m$ [171]
B	$250 \pm 15\ \mu m^3 s^{-1}$	$60000\ \mu m^3 s^{-1}$ [171, 172, 59]

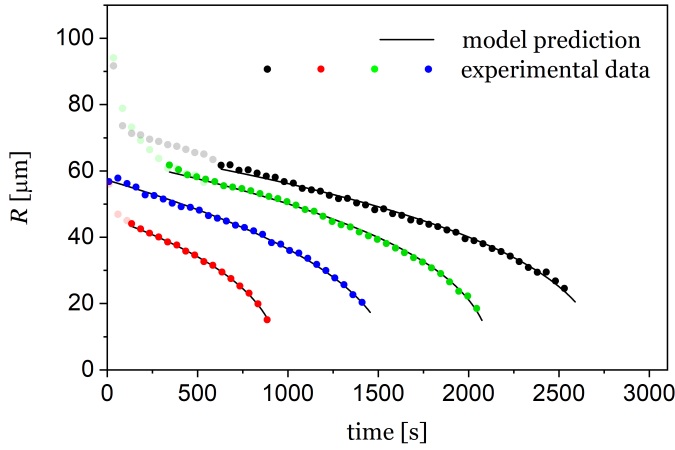


Figure 3.9. Bubble dynamics of dissolving bubbles. Experimental data and results of fitting with the Epstein and Plesset model [167, 168]. The experimental data are referred to the dissolution curves of Figure 3.6.

Focus on bubble coalescence

Bubble coalescence is the process by which two (or more) gas bubbles in close proximity merge and form one larger bubble [176]. When two bubbles approach each other, a thin film of polymer/gas solution is formed. The thin film can assume different shapes and go through different deformation dynamics, depending on the viscoelastic properties of the polymer/gas solution, the relative dimension of the bubbles and the velocity with which the two bubbles approach each other [29, 177].

In the simple case of two impinging bubbles of almost the same size in which the viscoelastic effects are negligible, the thin film is flat (Figure 3.10a). The polymer/gas solution is squeezed out of the thin film, pushed by capillary pressure, and undergoes a biaxial elongation [178]. When the strain rates are higher and the viscoelastic effects are relevant, the thin film assumes a parabolic shape, extending into one of the bubbles, before rupture occurs (Figure 3.10b). In this study, even higher deformation rates are observed and novel coalescence patterns are observed, in which the thin film is highly elongated inside one of the who bubbles (Fig-

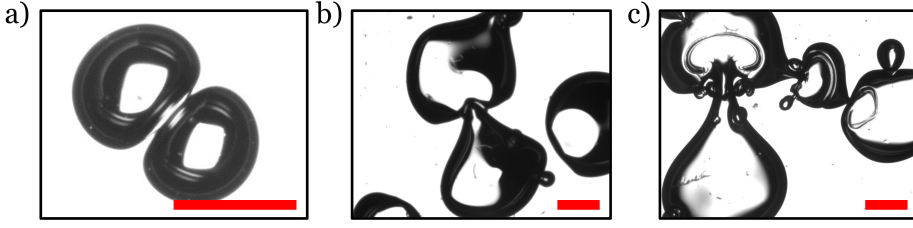


Figure 3.10. Observed coalescence patterns. The shape of the thin film between the bubbles can be: (a) flat; (b) parabolic; (c) elongated inside one of the two bubbles. Scale bar is $500 \mu\text{m}$.

ure 3.10c). Additional research is required to elucidate the physics that govern these new patterns.

Once the two bubbles establish contact, the film rupture occurs and a ring-shaped neck is formed [179]. First, this expands rapidly, due to the relaxation of the elastic energy built up during bubble expansion [180]. Then, the high curvature of the neck leads to the generation of a considerable capillary pressure, which, at this point, drives the neck expansion against inertial and viscous forces. The resulting expansion progresses with the following scaling law [181, 182, 183]:

$$\frac{r_n}{R} = K \left(\frac{t}{\tau} \right)^\alpha, \quad (3.12)$$

where r_n is the radius of the neck, K is the scaling law factor, τ is the characteristic time that can be inertio-capillary $\tau = (\rho R^3/\gamma)^{1/2}$ or visco-capillary $\tau = \eta R/\gamma$, and α is the scaling law exponent [181]. The characteristic time scale depends on the relative importance of inertial and viscous effects, which can be estimated by the Ohnesorge number, $Oh = \eta/\sqrt{\rho\gamma R}$.

Figure 3.11 reports characteristic images of the coalescence of two bubbles of almost the same size in the case of the PP/N₂ system, at a temperature of 180 °C and a pressure of 4.0 MPa. Figure 3.11 also reports, for several couples of coalescing bubbles, the normalized neck radius r_n/R , against the dimensionless time t/τ , where $\tau = \mathcal{O}(10^2 \text{ s})$ is the visco-capillary time (with $Oh = \mathcal{O}(10^5)$). Data for each coalescence event follow the power law with an exponent $\alpha \approx 1$, for the $t/\tau < 2$ s, decreasing to 1/4 for longer

times, which is similar to what was reported in the literature. In particular, the evolution of the neck in water-based systems has been observed to follow a power law with an exponent $\alpha \approx 1/2$ for $t/\tau < 0.2$, after which the exponent decreases [183, 181]. In viscous liquid systems, the evolution of the neck is significantly slower but follows the same dynamics, with $\alpha \approx 1/2$ [182].

The analysis of the coalescence patterns, together with the evolution of the neck, represents a powerful experimental platform to characterize the system, as it involves both interfacial tension and viscoelastic properties of the polymer/gas solution. In this framework, control over the occurrence and velocity of coalescence, triggered by the growth stage, is crucial.

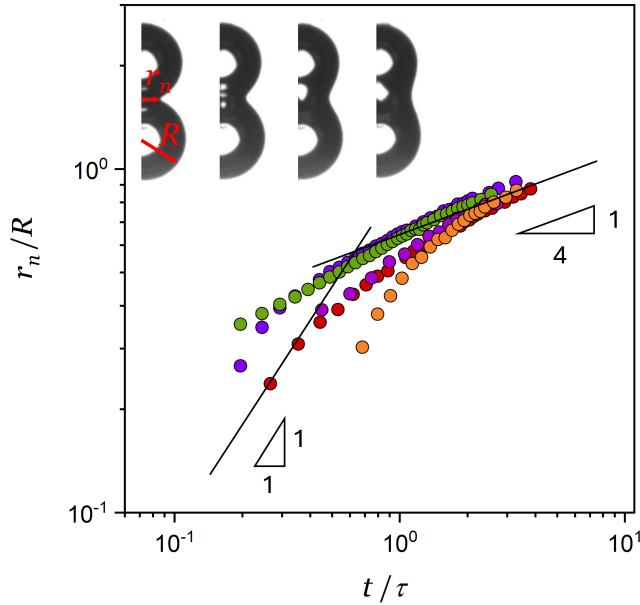


Figure 3.11. Coalescence of two bubbles of almost the same size in a PP/N₂ system, at $P = 4.0$ MPa. Evolution of the normalized neck radius (r_n/R) against the dimensionless time (t/τ).

Focus on bubble shape variation

Bubbles interaction causes the bubble shape to change from a spherical to a polyhedral one. Figure 3.3d shows two images with a bubble highlighted, subject to shape variation due to the presence of other proximal bubbles and the temporal evolution of RND of the same bubble. Initially, $RND \approx 1$ as the bubble is small and isolated. With bubble growth, it impinges on proximal bubbles and the shape changes (with the observed decrease in RND). The minimum in RND corresponds to the left image in Figure 3.3d. Driven by interfacial tension, eventually, the system slowly returns to a spherical shape and RND tends to one. The observed time scale of the phenomenon agrees with the visco-capillary time, $\tau = \mathcal{O}(10^2 \text{ s})$ (see Paragraph *Focus on bubble coalescence*), when major shape change occurs. When the curvature approaches $1/R$ the driving force for the shape variation is no longer related to the capillary effect, slowing the kinetics [182]. A detailed description of the corresponding dynamics and the relative descriptive model is left for future work.

3.3.3 Periodic treatment

Controlling the dynamics of bubble growth by applying a given pressure treatment can be used to tailor the morphology of a multi-bubble system. We demonstrated in the previous sections that we can control the amount of nucleated bubbles and their final radius by modulating the pressure. We will now show how to modulate the bubble relative position towards a total control of the foam features. Here, we exploit polymer viscoelasticity and apply periodic pressure treatments to determine non-reversible movements (in terms of d) among the bubbles. Two impinging bubbles are subjected to forces which are normal to the plane that separates them (or parallel to d). In particular, when they grow, they are pushed more far apart (d increases), and when they shrink, they are brought closer. Any imbalance may induce a permanent change in d , in principle at constant R . To do so, we imposed a negative pressure change $\approx 1 \text{ MPa}$ within a characteristic time $\mathcal{O}(10^2 \text{ s} \gg \tau)$ and a positive pressure change with an identical absolute value but within a characteristic time $\mathcal{O}(10^0 \text{ s} \approx \tau)$. The presence of the elastic contribution of the polymer response in only one of the two stages gives the desired imbalance. As expected in a viscous polymer/gas system under

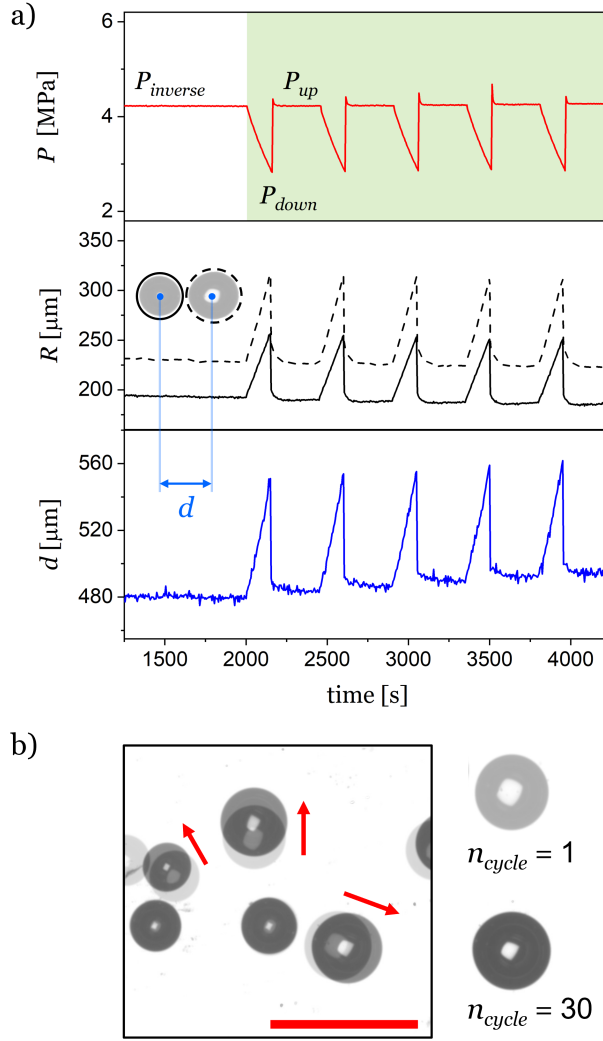


Figure 3.12. Effect of the periodic pressure treatment on the bubble relative position. Representative parts of (a) Periodic pressure treatment (red), bubble radius evolution (black), interbubble distance (blue). (b) Comparison of bubble positions after 30 cycle. Scale bar is $1000 \mu\text{m}$.

typical processing conditions, the change in d is small. However, repeating the sequence may induce an arbitrarily large movement. Figure 3.12a shows the temporal evolution of P , R and d in a treatment with 30 cycles, inducing a bubble movement depicted in Figure 3.12b, with the largest net increase in the distance between bubbles $\approx 70 \mu m$.

3.4 Conclusions

We introduced the inverse pressure quench treatment on nucleated polymer/gas systems to manipulate bubble growth dynamics. This allows for broadening the observation window and, thoroughly investigating the numerous phenomena and material properties related to bubble growth. By focusing on the model system PP/N₂, we reported using of the treatment to decouple bubble nucleation and growth, towards the design of foams with a defined **number density** and **size** of bubbles. Furthermore, the treatment proved suitable for studying bubble impingement, Ostwald ripening, and bubble coalescence. We foresee using of the same to measure the physical properties of polymer/gas systems, as we showed for the variables utilised in the Epstein and Plesset model for the diffusion-controlled dissolution of isolated bubbles. Finally, by using a periodic pressure treatment, we show that it is possible to move the bubbles and design their **relative position**, towards total control of all the foam features, opening novel opportunities for the design of foam processing technologies. This approach could be further explored for industrial applications, such as large-scale production of porous membranes for separation processes, scaffolds for tissue engineering, as well as thermal insulators and electrodes. Finally, to build on the findings of this study, future research could explore the exciting overshoot (undershoot) observed after a pressure step decrease (increase) (see Figure 3.7).

Chapter 4

Porous membranes produced via physical foaming

4.1 Introduction

Polymeric porous membranes with nanometric thickness, which have pore size ranging from nanometers to micrometers, received growing interest as they find extensive use across various applications, namely separation membranes [184], photonic devices [36], bio-materials [185], and template for crystal formation [96, 186]. Actually, the use of these films depends strongly on their morphology, namely cells size, shape, distribution and type of cell structure (closed cells, open cells, or a mixture of both). Various fabrication methods have been exploited to produce microporous membranes, such as breath figure, directional freezing, and self-assembly of block copolymers [2, 37].

Polymer physical foaming, via pressure induced phase separation, is a viable alternative for the production of porous membranes, standing out for its simplicity, possibility of scaling up and low environmental impact, in contrast to the above-mentioned techniques, which are expensive, limited to the small scale (microns or centimetres), and generate a large amount of organic solvent waste.

However, adapting the polymer foaming technique for the production of porous membranes and, in general, for products characterized by at least one micrometric or nanometric dimension (nanoparticles, fibers, or thin films) is not trivial. In these cases the blowing agent (BA) can easily dif-

fuse out from the polymer matrix, rather than forming bubbles [1]. Bubble nucleation occurs few seconds after the achievement of the supersaturated condition and, during this time, namely nucleation induction time (τ_n), BA molecules can escape from the surface. As a consequence, a dense polymer layer is formed, whose thickness (δ) corresponds to the diffusive path available to BA molecules before nucleation occurs ($\delta = (D\tau_n)^{1/2}$) [53]. Typically, the available diffusive path is larger than a micron, which means larger than the characteristic dimension of the above mentioned products. To overcome this issue we need to hinder the gas escaping.

One proposed strategy is the use of a different BA, for instance, with a smaller diffusivity (D). In this way the diffusive path can be reduced, making it smaller than the characteristic dimension of the sample. However, exploiting this strategy will always lead to the formation of a non-foamed layer, which might limit some applications that require open bubbles on the surfaces. A more effective strategy is the use of a barrier to prevent gas diffusion and constrain the gas to segregate forming bubbles. The barrier might be a polymer with a smaller diffusivity than the one of the polymer we want to foam [187, 50]. Li et al. [51] proposed a method to produce micrometric thin polymeric porous films with supercritical CO₂, Siripurapu et al. [52] used a CO₂ impermeable barrier attached to a micrometric thin film surface of poly(methyl methacrylate) (PMMA), and Orsi et al. [53] created hollow nanoparticle by gas foaming including the raw particle in a polymer matrix with a very low CO₂ diffusivity.

The objective of this chapter is to extend the use of the above mentioned approach, by pushing its applicability to film with nanometric thickness rather than the micrometric one. To this end, the use of a gas barrier to foam a nanometric thin film of poly(lactic-co-glycolic) acid (PLGA) has been tested. Furthermore, the phenomena involved in the cell morphology build-up in such a confined system will be elucidated. Finally, a novel approach to gain control over the final cell morphology will be proposed.

4.2 Materials and methods

4.2.1 Materials

PLGA 50:50 Resomer (®)RG 504 ester terminated M_w 38,000-54,000, polyvinyl alcohol (PVA) Mowiol (®)18-88 M_w 130000, and dimethyl carbonate (DMC) were purchased by Sigma-Aldrich (St. Louis, Missouri, United States). Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) (Clevios™HTL Solar) and indium tin oxide (ITO) glass covered substrates ($2.5 \times 2.5 \text{ cm}^2$) were purchased by Ossila©(Leiden, Netherlands). CO_2 and N_2 (purity 99,99 %) were supplied by SOL S.p.A. (Monza, Italy).

4.2.2 Film preparation

Spin coater (Ossila©, Leiden, Netherlands) was employed for the fabrication of the polymeric thin films. The PEDOT:PSS which was used as the sacrifice layer, was deposited using a spin speed of 3000 rpm for 30 s dripping and spreading the solution in static condition. After the spin coating, the film was annealed at 90°C for 20 min to allow full evaporation of the solvent. The PLGA deposition method was optimized for the production of an uniform film (see appendix B). It was produced via spin coating of a solution of PLGA in DMC 5 %w/w with a spin speed of 5000 rpm for 60 s dripping the solution in static condition. The barrier layer of PVA was deposited on the top of the PLGA film via solution casting, using $300 \mu\text{L}$ of a solution of PVA in deionized water 10 mg/mL. Finally the film was dried at ambient temperature overnight (Figure 4.1) Morphology analysis was performed using an optical microscope Stemi 208 (ZEISS, Oberkochen, Germany) and a scanning electron microscope (SEM) FEI Quanta 200 FEG (Hillsboro, Oregon, United States).

4.2.3 Porous membranes fabrication via physical foaming

The gas foaming experiments were performed with a custom-made foaming apparatus which is detailed described elsewhere [188]. It consist in a pressure vessel (0.3 L in volume, BC-1, High Pressure Equipment Co., Erie, PA, USA), equipped with heating elements controlled by a

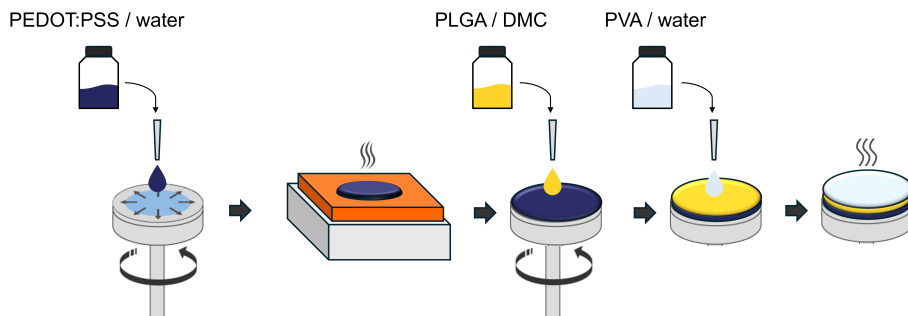


Figure 4.1. Thin film layers fabrication scheme.

PID thermoregulator (1850, Gefran S.p.A., Provaglio d’Iseo, Brescia, Italy). The pressure and temperature are monitored respectively with a pressure transducer (mod. TK, Gefran S.p.A., Provaglio d’Iseo, Brescia, Italy) and a thermocouple positioned as close as possible to the samples (Pt100, Gefran S.p.A., Provaglio d’Iseo, Brescia, Italy). The pressure discharge system consists of a ball valve (15-71 NFB, High Pressure Equipment Co., Erie, PA, USA) and an electromechanical actuator (15-72 NFB TSR 8, High Pressure Equipment Co., Erie, PA, USA) to ensure a controlled and repeatable pressure reduction rate. The foaming process consists in the solubilization of the BA, namely CO_2 , at 100 bar and 80 °C for 2 hours. This time is overestimated to allow for the gas diffusion towards the PVA barrier. Phase separation is induced by rapidly reducing the pressure to ambient pressure. Finally, the film is extracted and soaked in diluted water overnight to wash out the PVA and PEDOT:PSS film so that it can be suspended in water for further manipulation (Figure 4.2).

4.3 Results and discussion

4.3.1 Diffusion restricted physical foaming

The foaming process of PLGA film with a nanometric thickness was examined. The film before foaming has a thickness of approximately 400 nm (see Appendix B), which is significantly smaller than the diffusion length of CO_2 through PLGA during the nucleation induction time, estimated to

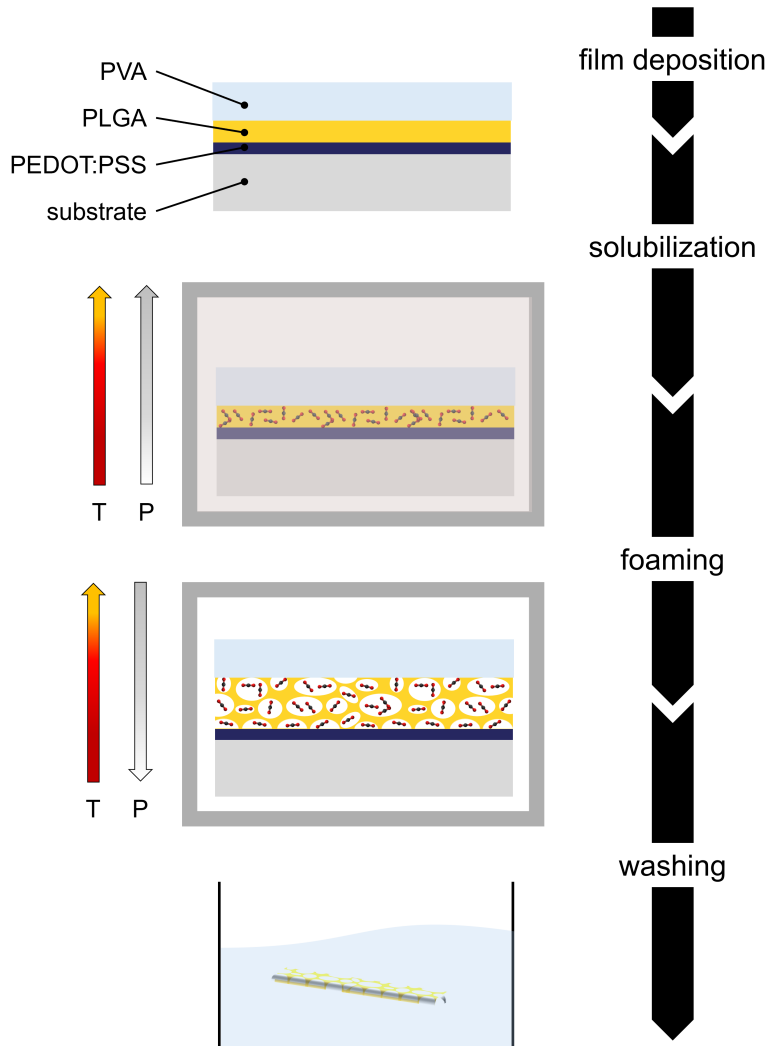


Figure 4.2. Porous membranes fabrication scheme. The multi-layer structure is foamed via physical foaming. Finally the porous membrane is suspended in water for further manipulations.

be around $L = 1000\mu m$, considering $D = 10^{-7}cm^2/s$ [189], and τ_n equals

to the pressure reduction time $\tau = 0.2s$. Therefore, employing a gas barrier is crucial, as confirmed by experimentally foaming a sample partially covered with the PVA barrier illustrated in Figure 4.3. The polymer film is transparent before treatment and remains so in regions without the barrier. However, in areas where the barrier is applied, the film turns white and shows reduced transparency due to the formation of a cellular structure responsible of scattering the light (Figure 4.3b).

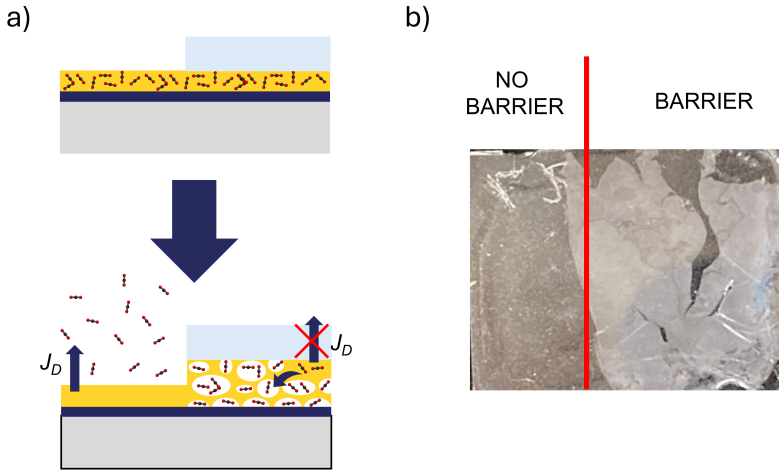


Figure 4.3. (a) Effect of the gas barrier scheme, bubble are only formed underneath the PVA barrier, as the blowing agent cannot escape from the film surfaces. (b) Evidence of the effect of the barrier, the presence of bubbles is evident from the color change of the film from transparent to white.

Eventually, the PLGA porous membrane is removed from its substrate by soaking the multilayer structure in diluted water, which dissolves the PEDOT:PSS and PVA layers. As depicted in Figure 4.4, the film floats with a crumpled appearance in the water bath. This indicates that the film possesses enough rigidity to remain free-standing in the liquid. However, a strategy for unfolding the membrane is required, thus enabling proper handling, such as mechanical testing or deposition on a substrate. One potential method involves a multiphase interface with a polar and a non-polar liquid, possibly causing the film to self-flatten at the interfaces [190].



Figure 4.4. Picture of a free standing porous membrane suspended in diluted water.

4.3.2 Morphology characterization

The microstructure of the porous membranes is shown in [Figure 4.5](#) and [Figure 4.6](#). As indicated by the SEM analysis in [Figure 4.5](#), it displayed a single layer of elliptical cells in the cross section. This is likely due to the manometric confinement [\[191\]](#), which constrains the bubble growth in the planar direction. In addition, the interface plays a critical role in facilitating bubble nucleation compared to the bulk, as explained by the heterogeneous nucleation theory [\[192\]](#). In the cases of multiple surfaces, namely PEDOT:PSS and PVA, the heterogeneous nucleation is more efficient on the surface by which the gas has a better affinity, as shown by the cross section analysis, in which the bubbles are open on the PEDOT:PSS side instead of the PVA one.

The SEM images of the top view of the membranes complete the cell structure analysis ([Figure 4.6](#)). Different bubble structures were observed when foaming under the same conditions of temperature, pressure and pressure reduction rate. In [Figure 4.6a](#) we can identify a cellular structure with darker zone that corresponds to the holes in the cell upper walls, and lighter zone corresponding to the cell lateral walls. The lack of resolution suggests that the cells are closed on the top side (in contact with the PVA

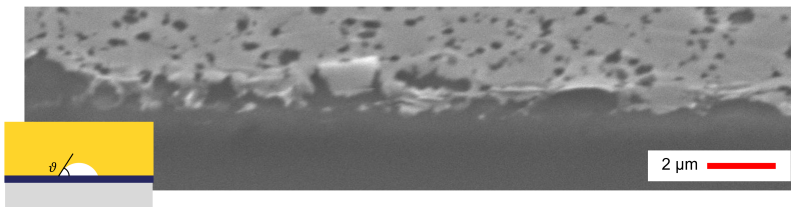


Figure 4.5. SEM images of the cross section of a porous membrane. The cells are open on the bottom side, in contact with the PEDOT:PSS, while are not fully open on the top side.

layer), while some round holes are well defined as the upper cell walls are damaged. The shape of the cells is regular, with a round or polygonal shape and an average diameter of $6.9 \pm 1.3 \mu\text{m}$. However, in [Figure 4.6b](#) the majority of the cells are well defined and open on both sides, while there are fewer cells that are closed at the top with small round holes in the center. The cell shape is irregular, characterized by corrugated cell walls, with an average cell diameter of $10.3 \pm 2.0 \mu\text{m}$. The increase in bubble diameter, as well as the irregular shape, is always evident when the cells are open on both sides of the film. In order to understand these differences in the morphology when foaming at the same condition, a deeper understanding of the phenomena involved in the cell structure build up is required.

To address this issue, the details of the cell morphology of several samples produced by different experiments under the same foaming condition are reported in [Figure 4.7](#). Four different cell patterns can be identified: (i) closed cells with groups of collapsing small holes on the upper cell walls ([Figure 4.7a](#)), (ii) closed cells with rounded holes on the upper cell walls, smaller than the cell size ([Figure 4.7b](#)), (iii) open cells with a collapsed upper wall characterized by several holes connected by a polymeric filament, characteristic of a coalescence patterns ([Figure 4.7c](#)), (iv) open cells with corrugated side walls ([Figure 4.7d](#)), recalling a not fully relaxed polymeric neck after coalescence. From a morphological point of view, the larger size of the cells when they are open, as well as the singular cell pattern, can be described as the consequence of early cell coalescence [13], as well

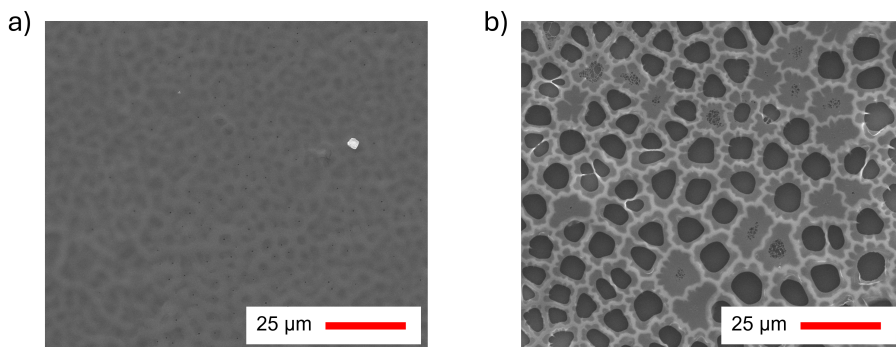


Figure 4.6. SEM images of the top view of the porous membranes. Images of two different membranes produced at the same foaming condition, (a) upper closed cells, (b) open cells on both side of the film.

as the rupture of the upper cell wall in contact with the PVA layer. In fact, coalescence leads to an increase in cell diameter and to the collapse of the structure, which is not trivial for this confined system. Since the system is sandwiched between two layers, polymeric flows are constrained. Thus, the shape relaxation after coalescence is slowed down and the adhesion with the PVA layer prevent the collapse of the upper wall. This is also supported by the fact that this coarsening phenomena occurs after the pressure reduction, when the polymer is still above the glass transition temperature, likely during the sample extraction operation, which is the less controlled step of the process. This would explain the variety of the different patterns and the lack of control provided by the modulation of process parameters.

4.3.3 Coarsening driven physical foaming

The build-up of the foam morphology depends on the occurrence of different phenomena as described in [Chapter 3](#), namely bubble nucleation, growth, coalescence and Ostwald ripening. Typically, increasing or decreasing the temperature and pressure is the easiest way to control the number of nucleated bubbles and their growth [1]. Finally, the classical technologies are designed and optimized to avoid the occurrence of coales-

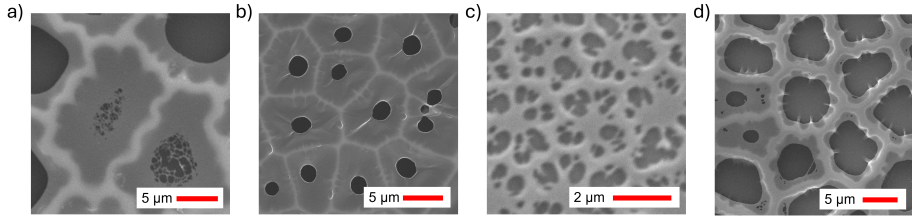


Figure 4.7. Porous membranes morphology details. (a) upper close cells with collapsing holes on the top side; (b) upper close cells with a rounded holes on the top side; (c) open cells with collapsed top walls with a typical shape resulting from coalescence; (d) open cells with a corrugated shaped lateral walls.

cence, which leads to the collapse of the cell structure and compromises the overall success of the foaming process [193, 194]. When foaming a nanometer sized film, the classical approach is not sufficient, as the bubble coalescence cannot be easily prevented, so novel approaches should be considered. The occurrence of the coarsening phenomena (i.e. coalesce and Ostwald ripening) is not fatal in this cases of a 2D structure, and does not cause a brutal density increase. Due to the confinement, the cell structure is supported on the top and bottom side, so the coarsening only causes the mean cell diameter to increase, without compromising the integrity of the membrane. Furthermore, several applications, like drug delivery [35] or filtration [2], require the cells to be bigger than the one obtained in the previous section and open on both side of the membrane. In this prospective the coarsening phenomena can be exploited to achieve open cells with a controlled final average diameter, similarly to the annealing step when producing solid crystals.

Herein, we propose a novel approach, namely *Coarsening Driven Gas Foaming*. This technique involves the imposition of the inverse pressure treatment proposed in Chapter 3, in order to limit bubble growth and obtain better control over cell coarsening. This allows us to introduce a new process parameter, the coarsening time, which corresponds to the time we keep the sample in the reactor after foaming at a certain pressure smaller than the saturation pressure. A proof of concept of the application of this technique is reported in Figure 4.8. In detail, to produce the porous

membrane in Figure 4.8b, after the pressure quench, the pressure is raised to 20 bar, and the temperature is kept constant throughout the process, for a coarsening time of 30 min. The cell morphology appears coarser compared to the one produced by the classical pressure quench treatment with a rapid sample extraction (Figure 4.8a). The average cell diameter is increased from $3.7 \pm 0.7 \mu\text{m}$ to $15.0 \pm 3.9 \mu\text{m}$ and the cell size distribution is more asymmetric [163]. The cell appears to be completely open on both sides of the film, with a circular shape, which is also a result of the coarsening effect reported in subsection 3.3.2. However, further analysis is required to confirm the effectiveness of this technique.

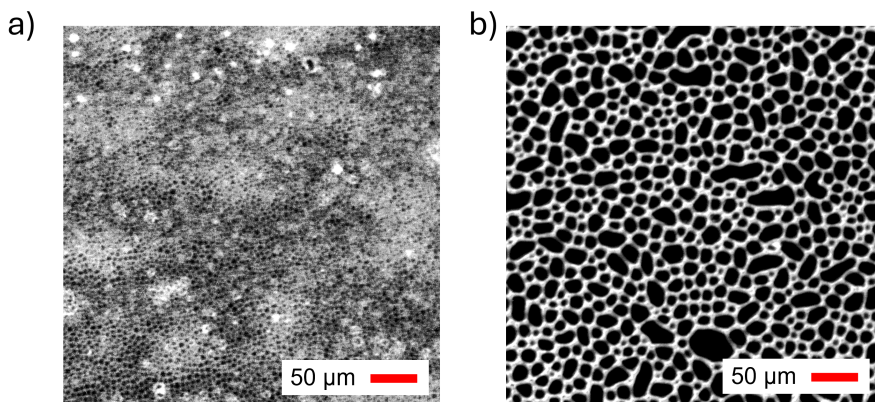


Figure 4.8. Microscope images of porous membranes produced (a) via pressure quench gas foaming, and (b) coarsening driven foaming procedure.

4.4 Conclusions

In this study, we explored the potential application of physical foaming techniques to produce nanoscale porous polymeric membranes, specifically focusing on PLGA films. By introducing a gas barrier layer, we effectively prevented gas diffusion from the film surface, enabling successful bubble nucleation and cellular structure formation.

The confinement demonstrates critical on the cell morphology build up,

where the nanoscale thickness limits bubble expansion primarily within the film plane. SEM analysis revealed a range of cell morphologies, influenced by heterogeneous nucleation and coarsening phenomena (i.e coalescence and Ostwald ripening), with some membranes showing closed cells and other open cells on the both side of the film. For the case of thin film embedded in a multilayer structure, coalescence and Ostwald ripening were not harmful to film stability and, in fact, this phenomena can be exploited to produce membranes with larger, open cells, which may be advantageous in applications like drug delivery and filtration.

Finally we proposed a novel approach named *Coarsening Driven Gas Foaming*, that consist in applying a controlled coarsening stage after the cells formation, proving effective in tailoring the cell size and structure. Future work will refine this approach, allowing for precise control over membrane porosity and enhancing the versatility of nanoscale porous membranes across various applications.

Chapter 5

Polymer assisted tin-based perovskite formation for optoelectronics

5.1 Introduction

Perovskite materials have granted significant attention in recent years due to their outstanding optoelectronic properties, making them ideal candidates for high-efficiency photovoltaic solar cells (PSC) [195, 62]. Traditionally, lead-based perovskites have been the most widely studied, but the toxicity of lead has stimulated research into alternative materials [63]. As a replacement for lead, tin element (Sn) is a promising alternative due to its similar electronic properties and lower toxicity [64]. However, the use of tin presents significant challenges, mainly due to its tendency to oxidation, from Sn(II) to Sn (IV), and the rapid non-radiative recombination of charge carriers [65]. The former derives primarily from environmental exposure, such as oxygen and moisture [67], while the latter depends on the intrinsic defects of the perovskite microstructure, such as iodide vacancies, tin interstitial, and lattice misalignment, that can arise if the crystal morphology development is not properly controlled [68].

The control over the passivation and the morphology of the tin-based perovskite crystals is essential for improving the stability and efficiency of devices. Several strategies have been proposed to address these issues, like additives engineering [196, 87], solvent engineering [197], and film-processing

engineering [198, 199] has shown promising results in enhancing film quality and stability.

Among the various strategies, the addition of polymers has proven to be a valuable approach, which is widely proposed for lead-based perovskite [200, 201, 84, 202, 203, 204], however, fewer examples have been reported for tin-based perovskites [89, 90, 91]. The polymer directly added into the perovskite precursor solution, modulates the crystallization dynamic, increases the viscosity of the precursor solution, and in contrast to small molecule additives, it remains immobilized after crystallization. Hence, it offers multiple benefits in perovskite films, suppressing ion migration, passivating defects, reducing interfacial recombination, improving stability, and regulating mechanical stresses [205].

Among all the proposed polymers, the pyridine based polymers [206] attracted our attention standing on the possibility of forming a Lewis acid-base adduct with the Sn(II) [207, 208], that may effectively retard the crystallization dynamic and passivate the grain defects [89]. The addition of low molecular weight pyridine derivatives, for instance, have been successfully employed to control the crystallization process, leading to improved film uniformity and reduced defects [209].

Herein, we propose a strategy to combine the effect of the pyridine functional group with the advantages of using a long chain polymeric additive. The influence of the polymer over the nucleation and growth step will be investigated, considering its effect on the morphology build up of the perovskite-polymer composite film. The design of a novel strategy to tune the device properties will be proposed, eventually, analyzing the final properties of the thus fabricated solar cell.

5.2 Materials and methods

5.2.1 Materials

Unless otherwise specified, all chemicals were employed directly without further treatment after purchase. Tin(II) iodide (SnI_2 , 99.99 % mesh), ethylenediammonium diiodide (EDAI_2 , >98%), N,N-dimethylformamide (anhydrous, 99.8%), 4-(tert-butyl)pyridine (tBP, 98%), Poly(2-vinylpyridine) (P2VP) (analytical standard, $M_w=159000$), Poly(4-vinylpyridine) (P4VP)

(Mw=160000), acetone (EMPLURA®), 2-PROPANOL (Riedel-de Haen) ($\geq 99.8\%$) Hellmanex, bathocuproine (BCP, 99.99%), and Silver beads (1-5mm, 99.9%) were purchased by Sigma-Aldrich (St. Louis, Missouri, United States). Formamidinium iodide (FAI, $>99.99\%$) was purchased by Dyenamo (Stockholm, Sweden). C60 (99.99%) was purchased by Solaris Chem Inc.©(Vaudreuil-Dorion, Quebec, Canada). Patterned Indium tin oxide (ITO) substrates ($2.5 \times 2.5 \text{ cm}^2$, $20 \Omega/\text{square}$) substrate and Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) (Clevious™HTL Solar) was purchased by Ossila©(Leiden, Netherlands). The PEDOT:PSS was filtered with a $0.22 \mu\text{m}$ PTFE filter before using.

5.2.2 Perovskite precursor solution preparation

A solution of SnI_2 in DMF with nominal molarity of 1.6 M was prepared and kept shaking overnight at ambient temperature. In a new vial FAI powder is scaled and a proper amount of the SnI_2 solution was added leading to a FA:Sn molar ratio of 0.95:1. In a new vial we scaled the EDAI_2 powder, and we add a proper amount of the final solution, after the complete dissolution of the FAI powder has been achieved (around 1 hour). We thus obtained a stock solution of $\text{FA}_{0.95}\text{EDAI}_{0.05}\text{SnI}_3$ in DMF. For the first part of the study we dilute the solution with a solution of DMF and the polymers with different concentration, ranging from 0.001 mg/mL to 100 mg/mL, leading to a final solution of 0.8M. For the second part of the study we analyze the mixed effect of the polymers and the tBP keeping the final molar ratio between the Sn and the pyridine equal to 0.6 n/n. Thus we dilute the stock solution with polymers reaching a 1.4M solution, and then we added the tBP accordingly to reach a final solution with a molarity of 0.8M. also in this case we evaluated the effect of the polymer concentration, ranging from 0.001 mg/mL to 1 mg/mL As a reference we used the same solution but diluted with tBP in a volume ratio 1:1.

5.2.3 Device fabrication

An inverted structure was employed for the PSCs fabrication, with the following layer sequence:
glass/ITO/PEDOT:PSS/ $\text{FA}_{0.95}\text{EDAI}_{0.05}\text{SnI}_3$ /C60/BCP/Ag. The indium

tin oxide (ITO) substrate was washed in sequential order with hellmanex dissolved in deionized water (2% v/v), deionized water, acetone, and isopropyl alcohol for 15 min each time under ultrasound conditions at 40 °C. Then, the ITO substrate was blow-dried with a nitrogen gun, followed by UV ozone treatment for 15 min. The PEDOT:PSS hole transport layer (HTL) was spin coated on the ITO substrate at 3000 rpm for 30 s and subsequently annealed at 90 °C for 20 min. The substrates were then transferred into a nitrogen-filled glovebox ($O_2 < 0.1\text{ppm}$, $H_2O < 0.1\text{ppm}$, temperature 18 °C) for all the following steps. A volume of 100 μL of the perovskite solution was deposited on the PEDOT:PSS surface, and spin coated at 3000 rpm for 60 seconds, and immediately annealed at 140 °C for 30 min. The C60 (ETL), BCP and the Silver electrode were deposited using a thermal evaporation chamber at a high vacuum ($< 10^{-6}$ mbar). The thickness of the three layers, C60, BCP and Ag, were 40, 7 and 140 nm, respectively. The effective area of each pixel of the perovskite device was designed to be 0.025 cm^2 .

5.2.4 Characterizations and measurements

For the following characterizations, the perovskite film were deposited on the PEDOT:PSS layer using the ITO covered substrate, and finally covered with a PMMA layer (20 mg/mL in toluene, 3000 rpm, 30 sec), to reduce the oxidation of the film during the measurement time. X-ray diffraction (XRD) was performed with a D8-Discover 25 diffractometer (D2 PHASER, Bruker, Billerica, Massachusetts, United States) at room temperature. Tescan Mira 3 scanning electron microscope (TESCAN GROUP, a.s., Kohoutovice, Czech Republic) operating at 5 kV, was used to investigate the morphology of perovskite films, for both top-view and cross-section images. Perovskite films were deposited on PEDOT:PSS layer on top of an ITO glass substrates to reduce charging problems and reproduce the same deposition process that is used for the device fabrication. A commercial platform (ARKEO) (Cicci Research Srl, Grosseto Italy) was used to conduct the characterization inside the glovebox on the final device. The device current density-voltage (J-V) characteristics were tested using a 12 LED solar simulator with a calibrated optical power density of 100 mW/cm^2 . PSC J-V characteristics were measured every 10 mV with a sample rate of 100 mV/s. External Quantum Efficiencies (EQE) were mea-

sured using a neon white light source with a monochromatic light, whose intensity was calibrated using a Hamamatsu S1337 Si calibrated photodiode.

5.3 Results and discussion

The use of pyridine based polymers proves to be an effective strategy for the production of high quality perovskite films, by exploiting the formation of a strong Sn-N complex [207]. The polymer acts as a strong templating agent, which slows down the crystallization process, drives the crystal growth in a preferred direction, adjusts the dispersion rheology, allowing thickness modulation, encapsulates the crystal grains and passivates their surface. Nevertheless, the combination of long polymer molecules and small pyridine molecules proves effective in improving the properties of the PSC device, allowing a stable anti-solvent free process.

5.3.1 Polymer perovskite compatibility

The FASnI_3 perovskite dispersion is prepared using DMF as a solvent, which is a good alternative to dimethyl sulfoxide (DMSO) to avoid the solvent-induced tin oxidation [81], and is compatible with pyridine molecules that are used as additives [209]. when used alone, DMF proves to be also a good solvent for the pyridine based polymer additives, namely, P4VP and P2VP [206]. However, the simultaneous addition of both the pyridine based polymer and the FASnI_3 precursors may affect their solubility. starting from a FASnI_3 dispersion 0.8M, the addition of P2VP and P4VP at different concentration has been tested, ranging from 0.01 mg/mL to 10 mg/mL, as shown in Figure 5.1. While the addition of P2VP does not influence the uniformity of the FASnI_3 dispersion, the addition of P4VP, at concentration higher than 0.047 mg/mL, causes the solution to become opaque, or even the formation of white precipitates. As a consequence, the solely effect of P2VP may be tested when using a polymeric additive alone. The fact that the dispersion is clear, with no evidence of particle, does not exclude the formation of complex aggregate on the nanometric scale, as the pyridine group attached to the polymeric backbone could interact and stabilize the colloidal perovskite nanoparticles [78, 77].

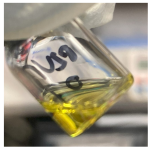
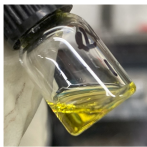
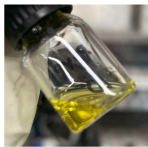
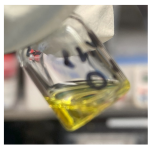
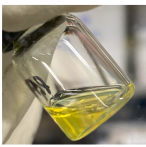
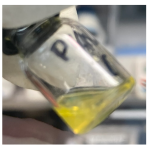
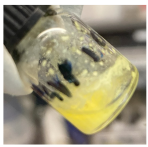
mg/mL	0.01	0.1	1	10
P2VP	 0.006	 0.062	 0.618	 6.43
P4VP	 0.007	 0.047	 0.493	 9.86

Figure 5.1. FASnI₃ polymer compatibility test of the perovskite solution 0.8M with different concentration of both P2VP and P4VP. The solution results opaque for concentration of P4VP higher than 0.047 mg/mL, while there is evidence of visible formation of white particle for higher concentration.

5.3.2 Film deposition process

There is no evidence of the effect of the polymer on the deposition process for concentration lower than 1 mg/mL, while, at higher concentration, the effect is distinct. The P2VP addition allows for highly reproducible antisolvent-free spin coating deposition process. In details, the crystallization process slows down, as the polymer concentration increases. The deposition process is schematically depicted in Figure 5.2, highlighting the impact of the polymer during the spin coating and the subsequent annealing step. We can identify the formation of the perovskite phase from the color transition of the film from yellow to gray/black. The FASnI₃ reference film turns grey during the spin coating, after approximately 20s (Figure 5.2a), while, the addition of P2VP 50 mg/mL, causes the film to turn red during the spin coating, and eventually black only during the annealing step (Figure 5.2b), eventually, with the addition of P2VP 100

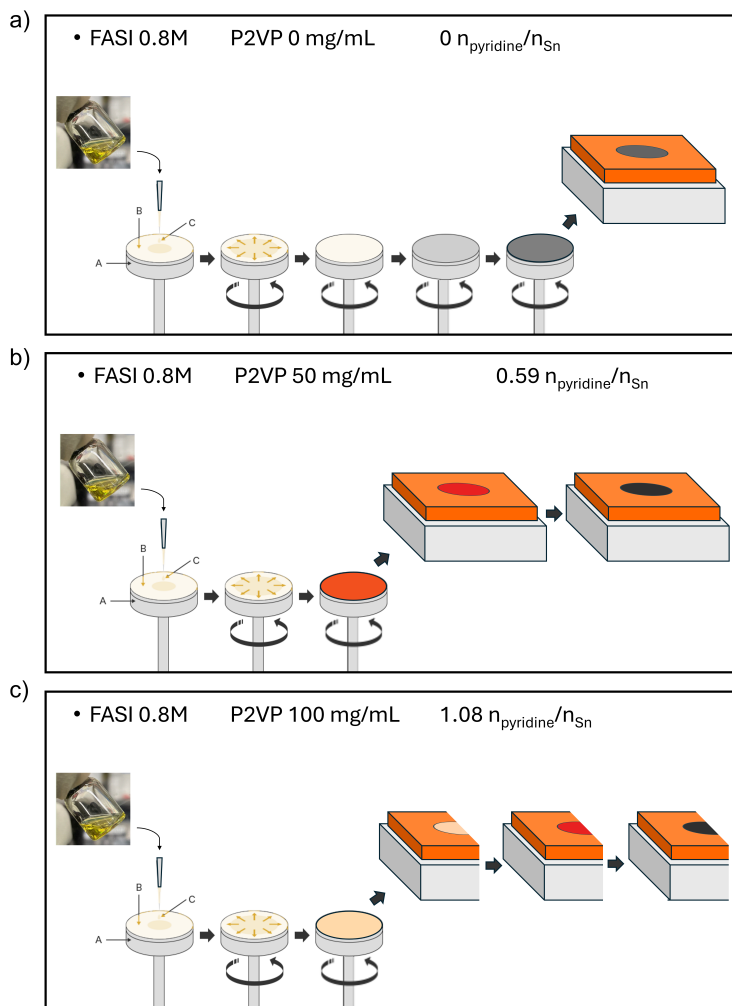


Figure 5.2. Deposition process scheme, namely, dispersion dripping, spin coating and annealing of (a) the reference film, and with (b) P2VP 50mg/mL, (c) P2VP 100 mg/mL. Effect of P2VP on the crystallization process is highlighted from the color transition of the film from yellow to red to black.

mg/mL the film remains yellow after the spin coating, and turns red and subsequently black only during the annealing process (Figure 5.2c). No strong effect of the spin speed and time has been observed.

The films produced after the annealing step are shown in Figure 5.3. With the increase in the polymer concentration, the film results black and lucid, instead of grey and opaque, confirming the production of a good quality film. The lucidity is related to the flattening of the roughness of the film surface, that is also detectable from the SEM images of the cross section (see subsection 5.3.4).

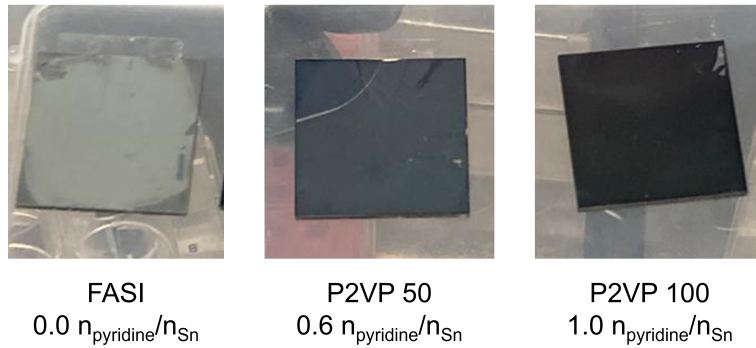


Figure 5.3. Picture of the film after the deposition process. Reference film appears grey and opaque (left), P2VP 50 mg/mL is black and opaque (center), P2VP 100 mg/mL is black and lucid (right).

Film thickness measurements was carried out with SEM analysis of the cross section of the perovskite films. The increase in the polymer concentration results in an increase of the perovskite film thickness, namely 359 ± 51 nm for 30 mg/mL and $0.36 n_{\text{pyridine}}/n_{\text{Sn}}$, 636 ± 75 nm for 50 mg/mL and $0.58 n_{\text{pyridine}}/n_{\text{Sn}}$ and 1143 ± 35 nm for 100 mg/mL and $1.19 n_{\text{pyridine}}/n_{\text{Sn}}$ (Figure 5.4a). This can be attributed to increases in viscosity caused by the polymer [210], similar to the rheology modifier effect reported by Giuri et al. [203]. The modulation of the polymer concentration can be used as a processing tool for the thickness control. Figure 5.4b reports the effect the polymer concentration over the film thickness at different $n_{\text{pyridine}}/n_{\text{Sn}}$ ratio. Considering its effect on the crystallization (see subsection 5.3.3), we

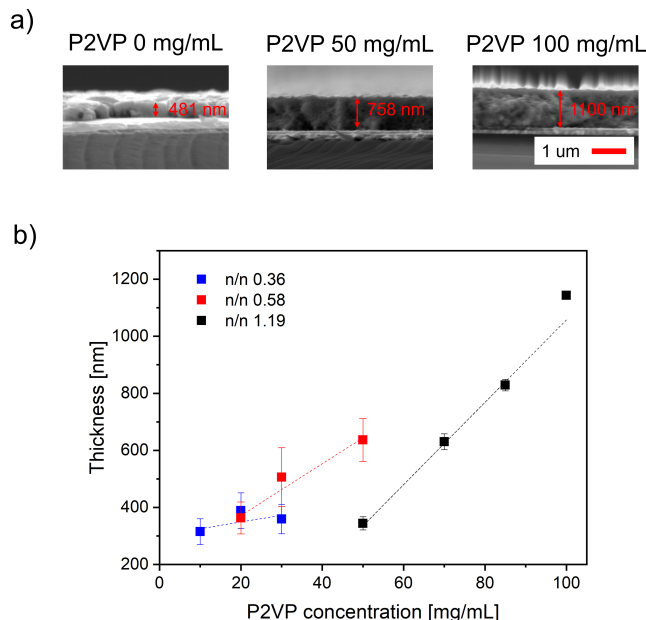


Figure 5.4. Perovskite film thickness analysis. (a) SEM images of the cross section of perovskite films with different polymer concentration; (b) effect of the overall polymer concentration on the film thickness at different $n_{\text{pyridine}}/n_{\text{Sn}}$ ratio, ranging from 0.36 to 1.19.

diluted with DMF the precursor dispersion after the addition of the polymer in order to keep the $n_{\text{pyridine}}/n_{\text{Sn}}$ constant (Figure 5.4b). This strategy allows for a thickness modulation for $n_{\text{pyridine}}/n_{\text{Sn}}$ bigger than 0.58, while for smaller amount of polymer the effect can be considered negligible. As a result, the polymer enables for a stable process, with a high repeatability, and the control over the thickness modulation [211], eventually facilitating the scalability of the solution-processed perovskite [73].

5.3.3 Crystal structure

The crystal structure of the perovskite composite film has been investigated by X-ray diffraction (XRD) analysis as shown in Figure 5.5. In the

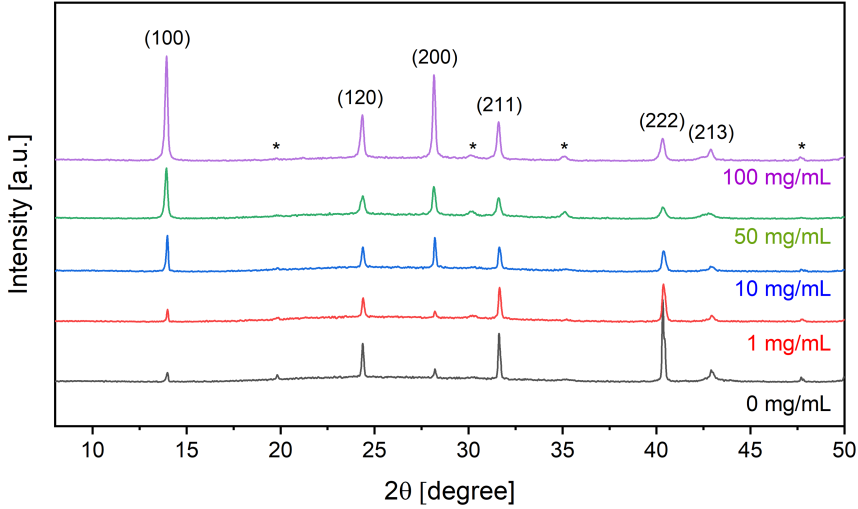


Figure 5.5. XRD patterns of the FASnI_3 and FASnI_3 -P2VP perovskite composite film with different concentration of polymer added in the precursor dispersion (0.8 M), namely, 1, 10, 50, and 100 mg/mL. (* marked peaks are referred to the ITO)

diffraction pattern of the FASnI_3 reference, six evident peak are present, at 14.0° , 24.4° , 28.1° , 31.6° , 40.4° , and 42.9° , corresponding to the crystallographic plane (100), (102), (200), (122), (222), and (213), which are typical of the perovskite orthorhombic crystal structure [212]. The peak position remains the same regardless the polymer concentration, thus we exclude any lattice deformation effect. Overall, the diffraction peaks intensity is enhanced accordingly to the polymer concentration, reaching an optimum at a P2VP concentration of 100 mg/mL, suggesting higher crystallinity. In particular the intensity of the peak referred to the principal direction (100) and (200), increases more with respect to the others, demonstrating that the templating effect of the P2VP can regulate the direction of grain growth. We evaluated the (100)/(120) peak intensity ratio that shows an increases almost exponentially with the polymer concentration, from 0.24 (reference film) to 1.96 (P2VP 100mg/mL) (Figure 5.6). This findings will also be supported by the SEM analysis, showing particular crystals shapes

(see [subsection 5.3.4](#)).

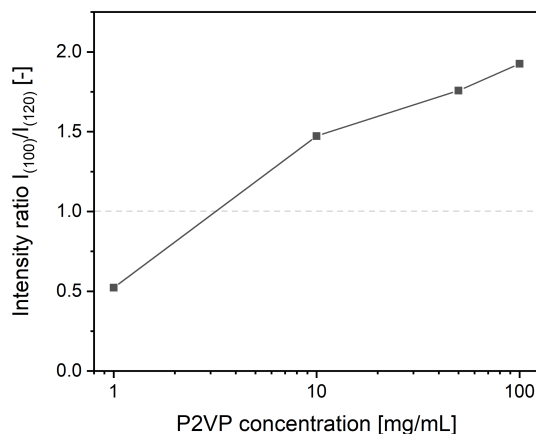


Figure 5.6. Peak intensity ratio, namely $I_{(100)}/I_{(120)}$ of perovskite (0.8 M) films treated with different P2VP concentrations (1, 10, 50, and 100 mg/mL).

5.3.4 Morphology characterization

The film morphology has been analyzed with SEM analysis, assessing the effect of the polymeric additive ([Figure 5.7](#)). As reported in similar work, the polymer cannot be embedded in the crystal lattice, and reasonably segregate on the grains surface [213, 214]. For the reference film, cubic-shaped perovskite crystals were observed, with incomplete substrate coverage. Evidence of the influence of the polymer is reported starting at a concentration of 1 mg/mL, where the perovskite crystals appear smaller. The SEM of the film with the addition of P2VP 10 mg/mL, shows a full coverage of the substrate, with a smaller grain size with respect to the reference, and with a surprising corrugated shape similar to a sort of self-assembled structure composing, or covering, the crystal grains. This strange structure could be the morphological evidence of the effect on the preferred crystal growth reported by the XRD analysis (see [subsection 5.3.3](#)). At higher polymer addition, namely 50 mg/mL, the SEM resolution decreases, facing difficulties in observing polymeric materials,

but an increase in the crystal size and a flattening of the surface can be observed, as deduced by the analysis of the film outcome and the cross section (Figure 5.3 and Figure 5.4).

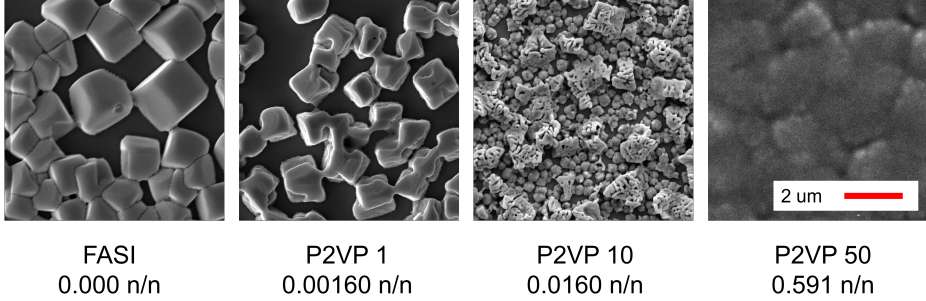


Figure 5.7. SEM images of the top view of the perovskite films of the reference film (FASnI₃) and with different amount a of P2VP added in a 0.8 M precursors dispersion.

The analysis of the cross section at high resolution provides a clearer view of the three dimensional structure of the film, as shown in Figure 5.8. The film is composed by elongated crystal grain, covered by a polymeric layer. Moreover, instead of the typical mono-layer of crystals grains, a true 3D packing of crystal grains, stacked one on top of each other, is observed. This confirms that the polymer significantly influences the crystal growth, leading to a very different shape than the typical cubic one (Figure 5.7).

In view of the application of the P2VP perovskite-polymer composite film, determining the thickness of the polymer layer that separates the perovskite grains is crucial. Based on the SEM analysis evidence, the grains are arranged in a 3D structure, which may modeled straightforward as a simple cubic lattice structure of perovskite cubes embedded in a polymeric matrix as depicted in Figure 5.8b. Considering a e b respectively the dimension of the perovskite grains and the thickness of the polymer layer dividing the grains, we can mathematically evaluate the ratio between the polymer and the perovskite volume (V_{P2VP} and V_{perov}) within the primitive cell of the model system (Figure 5.8c) as:

$$\frac{V_{P2VP}}{V_{perov}} = \frac{(a + b)^3 - a^3}{a^3}. \quad (5.1)$$

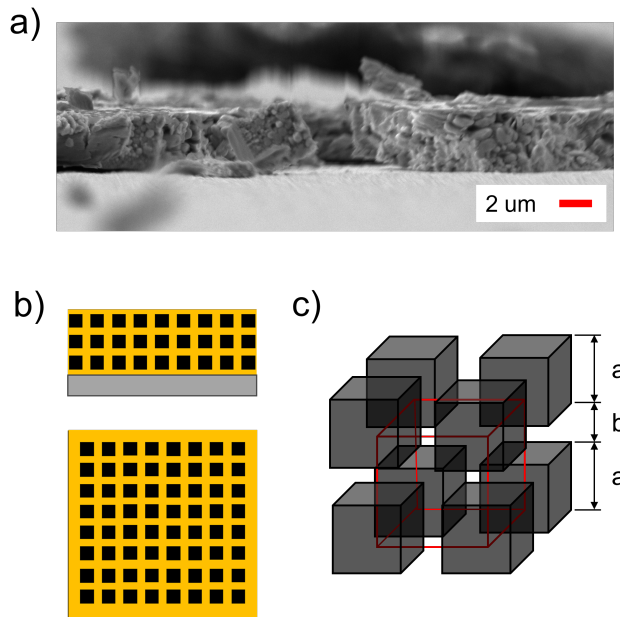


Figure 5.8. Morphology characterization of the perovskite P2VP composite film. (a) SEM of the cross section P2VP 50 mg/mL ($n_{\text{pyridine}}/n_{\text{Sn}} = 0.58$). (b) Morphology model representation.

Considering a grain size of 500 nm, for a P2VP concentration of 50 mg/mL, the polymer layer thickness is approximately 30 nm, which is greater than the tunneling limit and therefore impedes current flow [215]. In fact, the associated PSC device reports a null short circuit current density (J_{sc}), as will not be reported in subsection 5.3.5. To overcome this problem, referring to the above model, there are two ways in which we can reduce the thickness of the polymer layer separating two grains: reducing the grain size or reducing the amount of polymer, neither of which is feasible.

To keep the $n_{\text{pyridine}}/n_{\text{Sn}}$ ratio high enough to allow for the crystal growth templating effect, by reducing the polymer amount we used a mixture of polymer and a low boiling point pyridine molecule, namely tBP. As we can keep the polymer concentration low we tested both the P2VP and the P4VP effect (see subsection 5.3.1), taking advantages of the strong

interaction of the P4VP [207, 206] which could not been used alone as an additive.

5.3.5 Device performance

In view of applying the superior perovskite film, with preferentially oriented grains, a passivating agent on the grain surface, and produced with a more stable process, we have fabricated p-i-n PVSCs with the device architecture of glass/ITO/PEDOT:PSS/perovskite/C60/BCP/Ag, where the perovskite layer is $\text{FA}_{0.95}\text{EDAI}_{0.05}\text{SnI}_3$ with tBP (reference), a mixture of P2VP (0.1M) + tBP and P4VP (0.1M) + tBP. The J-V curves of the device are reported in Figure 5.9.

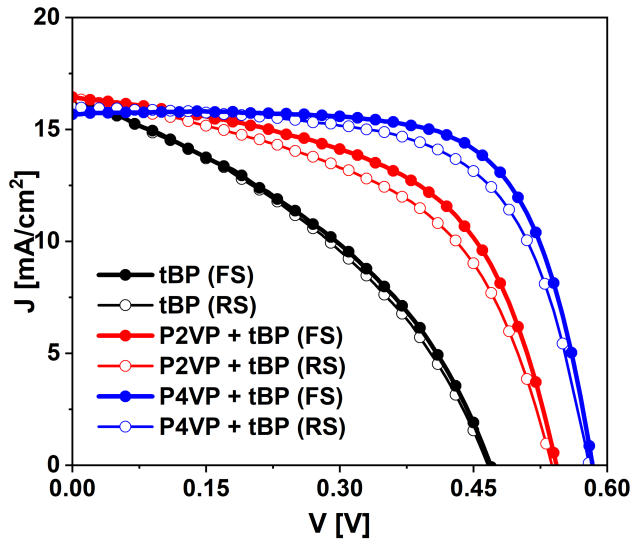


Figure 5.9. J-V curves of PSCs based on FASnI_3 with tBP and a mixture of P2VP+tBP and P4VP+tBP. The device are tested both in forward (FS) and reverse (RS) scan direction.

The reference film with tBP have a bad coverage of the substrate and shows poor reproducibility, with the best device showing a PCE value of 2.96%, an open circuit voltage (V_{OC}) of 0.47 V, a J_{SC} of 16.3 mA/cm^2 and a fill factor (FF) of 38.67% with a distinct hysteresis. On the contrary the PSCs devices with only the addition of polymer reports no current,

probably due to the insulating effect of the polymer, and therefore are not reported in Figure 5.10. Upon using the polymeric additive P2VP and P4VP at 0.1 mg/mL together with tBP in an amount to keep the total $n_{\text{pyridine}}/n_{\text{Sn}}$ ratio equal to 0.58, the device properties increases, with the P4VP proving to be the best additive.

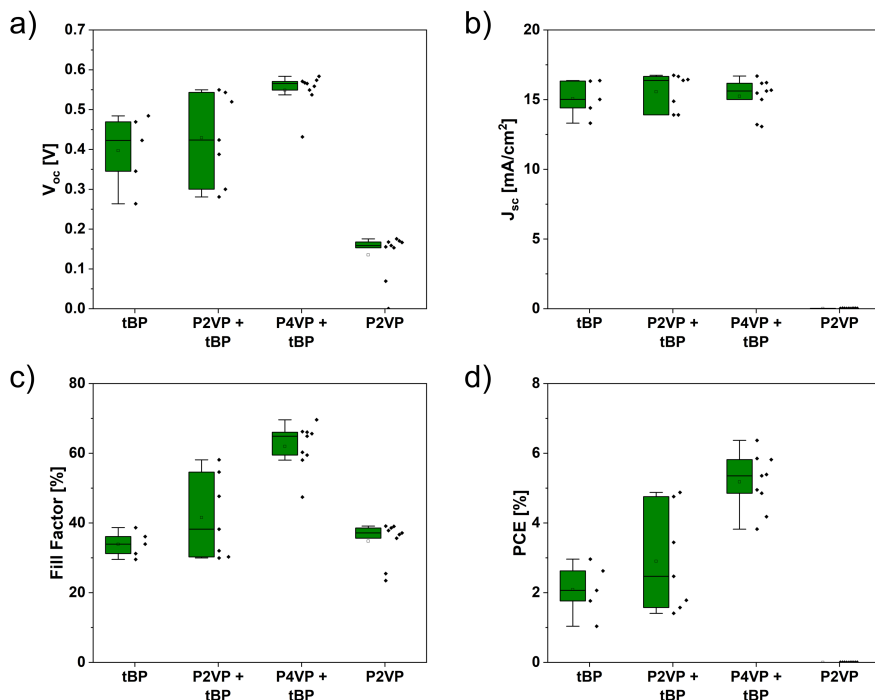


Figure 5.10. Characteristics photovoltaic performance parameters, namely (a) short circuit current density (J_{sc}), (b) open circuit voltage (V_{oc}), (c) fill factor (FF), and (d) Power conversion efficiency (PCE) for FASnI₃ 0.8 M based device processed with tBP, a mixture of P2VP+tBP, and P4VP+tBP. The plot highlights the distribution and variability of each property, providing insight into the impact of different additives on device efficiency and performance.

The V_{oc} , J_{sc} , FF parameters increase for the best device to respectively to 0.58 V, 15.67 mA/cm² (value confirmed by the integrated current density calculated from the EQE), and 69.62%, achieving a champion PCE

value of 6.37% (Figure 5.10). The use of polymer results in an effective antisolvent-free deposition technique, with an improved repeatability evident from the narrow range of efficiency histogram of Figure 5.10. However, there is still a lot of room for improvement, as a deeper analysis of the polymer concentration effect with the mixture strategy has to be analyzed, and the introduction of recently published strategies [81, 216, 217, 218], may be introduced in the presented protocol to improve the final device properties.

5.4 Conclusions

We explored the role of pyridine-based polymer additives, specifically P2VP, in enhancing the crystallization and performance of tin-based perovskite solar cells, exploiting the strong interaction between pyridine groups and tin ions (Sn-N complexes). While DMF proved to be a suitable solvent for these polymer additives, only P2VP demonstrated full compatibility in the FASnI_3 solution. Adjusting the polymer concentration allowed us to control the crystallization rate, modulate the surface roughness, and the film thickness. The addition of the polymer allowed for an antisolvent-free deposition process, which is highly reproducible. The polymer proves its potential in templating the crystal structure, inducing the formation of elongated grains encapsulated in a polymeric matrix, as confirmed by SEM and XRD analyses.

However, difficulties related to the polymer-induced increase in film thickness and the impact on charge transport were observed. To mitigate this, a strategy consisting in combining low molecular weight pyridine additives, namely tBP, with the polymer (P2VP and P4VP) was proposed. This approach allows to keep the optimal pyridine/Sn ratio, to ensure the crystallization templating effect, while reducing the polymer content. At an optimized polymer concentration, this approach led to a working device with overall increased properties, in a three times higher PCE with respect to the tBP alone, reaching with a more stable process the literature standard.

This work lays a foundation for future research into fine-tuning polymer-perovskite composites to optimize tin-based perovskite solar cells, potentially paving the way for more stable, efficient, and eco-friendly photo-

voltaic technologies.

Chapter 6

Conclusions

This thesis presents a comprehensive investigation into the mechanisms that drive the morphology build-up of a segregating phase during phase separation processes involved in the production of structured materials. The investigation is focused on two distinct systems: polymeric foams and tin-based perovskite-polymer composites. For each system, significant insights are provided into the mechanisms governing phase separation, namely, nucleation, growth, and coarsening. This contributes to the overarching aim of developing novel methods for structuring soft composite films at the micro and nano scales.

The impact of a liquid blowing agent, specifically Methylal, on the morphology of polymer foams was investigated. It has been demonstrated that methylal functions as an effective physical blowing agent for thermoplastic polyurethane (TPU), exhibiting high solubility. The combined use of Methylal and CO₂ led to a notable enhancement in the morphology of the foamed samples, characterized by a substantial increase in bubble number density, a reduction in average bubble size, and a decrease in densities. Additionally, Methylal has been observed to augment the foaming ability of conventional gaseous agents, facilitating the expansion of processing parameter windows and enhancing the stability and reproducibility of the process, which suggests promising potential for industrial applications.

To meet the challenge of a more precise control of the foam morphology, a deeper analysis of the phenomena involved in the build-up of the morphology was carried out in order to gain more tools for the design of new technologies. The *Inverse Pressure Quench* treatment was developed and proved to be effective in decoupling bubble nucleation from growth. This

approach allows a comprehensive analysis of numerous phenomena, namely bubble nucleation, growth, coalescence and Ostwald ripening, and allows bubble dynamics to be manipulated. Furthermore we designed a complex pressure treatment, namely the periodic pressure treatment, which exploits bubble interaction to modulate the relative position of the bubbles.

The design of these treatments not only allows to broaden the observation window for bubble dynamics, but also opens up opportunities to use the same to measure the physical properties of polymer/gas systems, or for improved foam processing technologies in various applications, including scaffolds for tissue engineering and thermal insulators. The uses of this novel designed approach has been proved. The fabrication of nanoscale porous polymeric membranes from PLGA films via physical foaming has been the subject of investigation. The introduction of a gas barrier layer has been demonstrated to be an effective method for the fabrication of nanoscale porous polymeric membranes via physical foaming. A comprehensive examination of the resulting foam morphology revealed that confinement exerts a profound influence on the morphology of the formed membranes. Additionally, the occurrence of early coalescence was identified as a significant factor that renders the conventional approach to morphology tailoring ineffective. It is therefore proposed that the combination of the inverse pressure quench with the diffusion barrier approach can be used to control the coarsening phenomena and exploit them as a morphology control tool, in a similar manner to that employed in solution processing crystal formation by the annealing process. The proposed approach, termed *Coarsening Driven Gas Foaming*, offers a promising avenue for the tailoring of membrane porosity and structure.

An investigation was conducted to analyze the solution processing of tin-based perovskite with the objective of developing new morphology control tools. The study investigated the impact of pyridine-based polymer additives on tin-based perovskite, demonstrating how these additives can facilitate crystallisation and regulate the formation of encapsulated crystals by leveraging the strong interactions with tin ions. The combined effect of a pyridine small molecule additive and a long-chain pyridine-based polymeric additive proved to be the most effective solution for improving the crystallization process and passivating surface defects. The optimized polymer concentration facilitated a reproducible antisolvent-free deposi-

tion process, leading to significant improvements in device efficiency. This work paves the way for further refinement of polymer-perovskite composites, which will in turn facilitate advancements in stable, efficient, and environmentally friendly photovoltaic technologies.

This research successfully underscores the driving mechanisms governing phase separation in each different system while addressing specific challenges in each application. The development of innovative techniques for the fabrication of soft composite films through a multidisciplinary approach has been well received. The proposed methods draw inspiration from the distinct approaches employed in two systems that appear to be disparate: polymeric membranes and perovskite composites. The innovative strategies introduced, including the inverse pressure quench treatment, the coarsening-driven foaming and the dual molecular weight additives, not only advance our understanding of material behavior under phase separation but also enhance the practical applicability of these materials in industrial processes. In conclusion, the results demonstrate a significant advancement in the design and control of structured materials, fulfilling the study aim and providing a solid foundation for future research into the optimization of micro- and nano-scale materials. The insights gained from the interactions of different phase separation mechanisms contribute to a broader understanding, inspiring impactful advancements in material science and engineering.

Appendix A

Bubble dynamic manipulation in polymer foaming

A.1 Rheological measurements

The linear viscoelastic properties of the polymer were measured at 180° using an MCR-WESP rheometer, Anton-Paar, Austria.

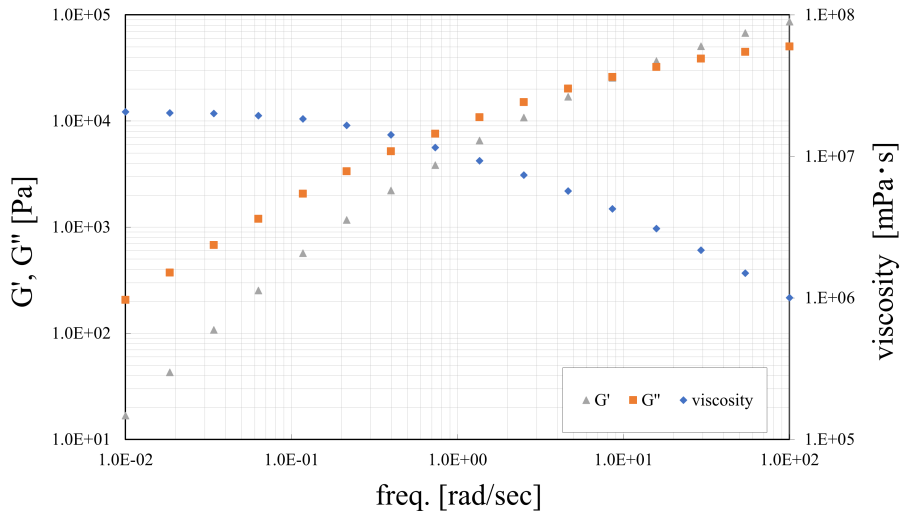


Figure A.1. G' , G'' , and viscosity (η) of polypropylene (PP) as a function of the shear rate.

Appendix B

Porous membranes produced via physical foaming

B.1 Spin coating parameter optimization

The spin coating optimization of PLGA/DMC solution was performed. The optimization involves the test of two spin mode, static and dynamic, several spin speed, ranging from 2000 rpm to 6000 rpm, and different the solution concentration, namely 3-5-8 % m/m (Figure B.1 and Figure B.2)

It was observed that film homogeneity improves as the spin speed increases and the PLGA mass fraction decreases. Furthermore, films made in the static mode shows higher homogeneity.

B.2 Film thickness measurement

Thickness measurement was carried out by profilometry analysis, using a Veeco Dektak 150 profilometer (Billerica, Massachusetts, United States) (Figure B.3. The PLGA film was fabricated via spin coating on a ITO covered glass substrate of a PLGA/DMC 5 %w/w solution using a spin speed of 5000 rpm for 60 s dripping the solution in static condition. The film was finally notched with a razor blade in the center.

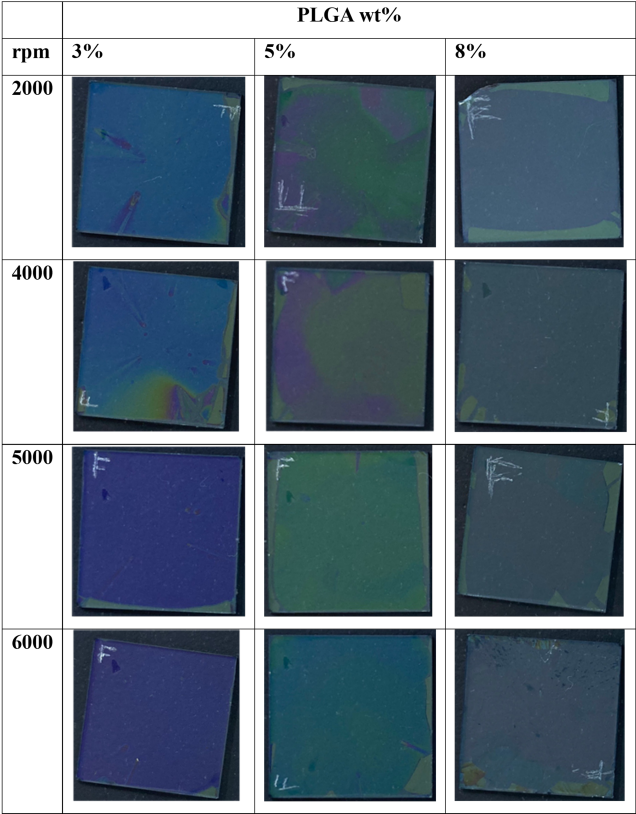


Figure B.1. Spin coating parameter optimization in static mode

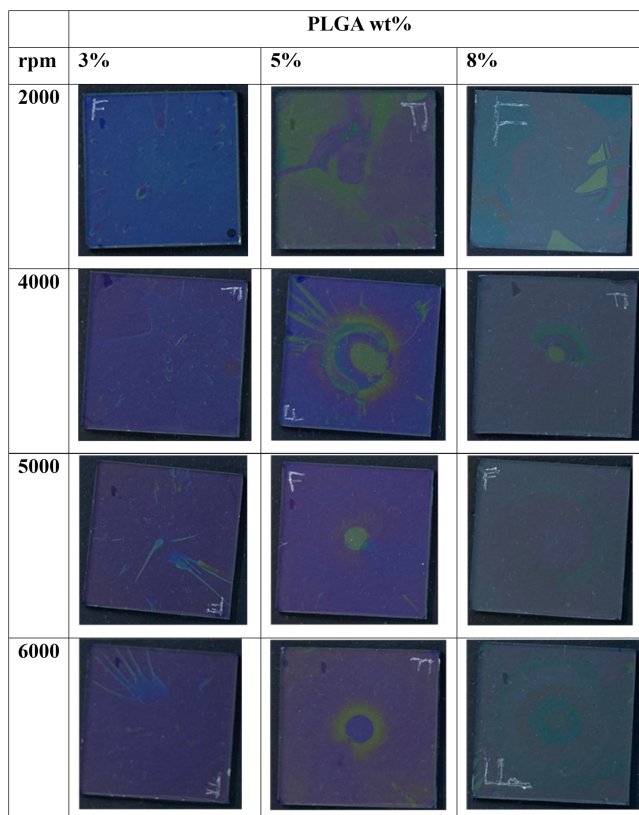


Figure B.2. Spin coating parameter optimization in dynamic mode

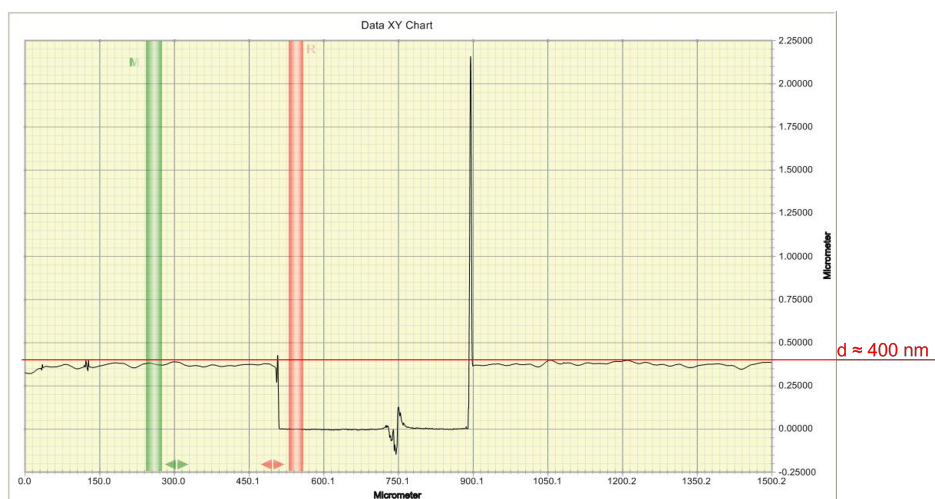


Figure B.3. Thickness measurement of PLGA film deposited via spin coating

List of Figures

1.1	Processing stages of a typical physical foaming processes. Reproduced with permission [1]. Copyright©2021 Elsevier B.V.	3
1.2	Polymeric foam morphology parameters with visual examples. Reproduced with permission [38]. Copyright©2006 The Royal Society of Chemistry. Reproduced with permission [39]. Copyright©2003 Materials Research Society. . . .	5
1.3	Perovskite crystals morphology characteristics with visual examples. Reproduced with permission [71], Copyright©2021 Wiley-VCH GmbH	8
1.4	Perovskite solution processing scheme. (a) Spin coating of perovskite precursor dispersion during which crystals nucleation and growth occurs, toward the formation of a wet film. Reproduced with permission [73]. Copyright©2021, Wiley-VCH GmbH. (b) Annealing step in which the coarsening of the crystals grains occurs. Reproduced with permission [74]. Copyright©2021 American Chemical Society	9
1.5	Possible nucleation and growth non-classical pathways. Reprinted with permission from AAAS [9].	10

2.1	Schematic of the experimental setup used for the liquid and gas foaming experiments where: (1) indicates the port connected to the termocouple; (2) indicates the port connected to the pressure sensor and the manifold; (3) indicates the viewing port, with a sapphire window, and (4) indicates the port used for the release of the PBA and concomitant expulsion of the samples.	21
2.2	(a) Pressure reduction over time; (b) moving average of central derivative of $P(t)$ (black) and central derivative of $P(t)$ (gray).	24
2.3	Vapor pressures of Methylal. Data represented with the full circles are taken from [125], data represented with the hollow squares are taken from [132] and data represented with the hollow circles are taken from [133].	28
2.4	Pictures of the sapphire window taken before (a) and after (b) foaming. Traces of material are visible on the glass surface in figure (b) as marked by the red dashed outline. .	29
2.5	(a) Pressure (normalized by the solubilization pressures) reduction curves of foaming experiment with gaseous blowing agent (dashed line) and liquid blowing agent (solid line) and (b) pressure reduction curves of liquid foaming experiments alone at different values of solubilization pressure.	30
2.6	PDR measurements: (a) effect of foaming temperature, solubilization pressure = 45 bar; (b) effect of pressure, foaming temperature = 132 °C.	31
2.7	Effect of temperature (a) and pressure (b) on the mean density of TPU foamed by the liquid foaming technique.	32
2.8	Morphology of the foamed TPU beads at constant pressure ($p = 45$ bar) and with varying temperature: (b) 122.2 °C, (c) 128.4 °C, (d) 132 °C and (e) 136.2 °C. Picture (a) is a larger-magnification copy of picture (c) and shows a sample with a varying morphology from top to bottom. This has been related to a minor varying temperature inside the vessel. .	34

2.9	Morphology of the foamed beads at the end of the liquid foaming experiments performed at constant pressure $p = 45$ bar and temperature (a) $T = 120$ °C, (b) $T = 136$ °C and (c) $T = 150$ °C. Morphology of the foamed beads at the end of the liquid foaming experiments performed at constant temperature $T = 133$ °C and pressure (d) $p = 30$ bar, (e) $p = 45$ bar and (f) $p = 60$ bar.	35
2.10	Density of foamed TPU beads at different values of foaming pressures and with different blowing agents: Methylal (black circles), Methylal + CO_2 (red circles) and CO_2 (green train-gles).	36
2.11	Morphology of TPU beads after the gas foaming experiment with the CO_2 /Methylal mixture (a,b) and with CO_2 alone (c,d) as the PBA. Pictures are taken at the center of the foamed beads (b,d) and on the boundary (a,c).	37
3.1	Visual observation apparatus scheme, with the pressure vessel and the details of the sample between two sapphire windows, the light source at the bottom and the camera above (left); general pressure treatment (right).	42
3.2	Bubble number density vs. pressure reduction at a fixed $P_{\text{sat}} = 8.1$ MPa. Scale bar is $1000 \mu\text{m}$	44
3.3	Bubble images reporting four different phenomena, namely, (a) diffusion driven bubble growth; (b) bubble dissolution caused by Ostwald ripening; (c) bubble coalescence; (d) bubble shape variation as a consequence of bubble impingement. For each phenomenon the left images report two subsequent frames separated by an arbitrary time interval. On the right, the representative parameter evolution. Scale bar $500 \mu\text{m}$	46
3.4	Inverse pressure quenching treatment: imposed pressure history (red) and bubble radius evolution (black); three different growth dynamics regimes corresponding to the pressure variation can be identified: first bubble growth (I), size reduction caused by the pressure increase (II), second bubble growth (III).	47

3.5	Pressure history of the inverse pressure quench treatment (red) and comparison with two simple pressure quench treatments (black and blue) and images of the sample at a $t = 20$ s. Scale bar is $1000 \mu m$	49
3.6	Inverse pressure quenching treatment outcomes. (a) Image of the sample after 25 s from inverse pressure quench ($P_{sat} = 8.1$ MPa, $P_{nucl} = 2.3$ MPa, $P_{inverse} = 4.8$ MPa) for isolated bubbles system. (b) Corresponding bubble radius evolution for all of the bubbles appearing in the image. (c) image of the sample after 25 s from inverse pressure quench ($P_{sat} = 7.3$ MPa, $P_{nucl} = 1.8$ MPa, $P_{inverse} = 2.3$ MPa) for interacting bubbles system. (d) Corresponding bubble radius evolution for all of the bubbles appearing in the image. Scale bar is $1000 \mu m$	50
3.7	Effect of bubble pressure on bubble growth dynamics. Imposed pressure history (red) and bubble radius evolution (black). The bubble inflate or deflate when the pressure is reduced or increased.	52
3.8	Effect of pressure variation velocity on bubble growth dynamics. Imposed pressure history (red) and bubble radius evolution (black).	53
3.9	Bubble dynamics of dissolving bubbles. Experimental data and results of fitting with the Epstein and Plesset model [167, 168]. The experimental data are referred to the dissolution curves of Figure 3.6	56
3.10	Observed coalescence patterns. The shape of the thin film between the bubbles can be: (a) flat; (b) parabolic; (c) elongated inside one of the two bubbles. Scale bar is $500 \mu m$	57
3.11	Coalescence of two bubbles of almost the same size in a PP/N ₂ system, at $P = 4.0$ MPa. Evolution of the normalized neck radius (r_n/R) against the dimensionless time (t/τ).	58
3.12	Effect of the periodic pressure treatment on the bubble relative position. Representative parts of (a) Periodic pressure treatment (red), bubble radius evolution (black), interbubble distance (blue). (b) Comparison of bubble positions after 30 cycle. Scale bar is $1000 \mu m$	60

4.1	Thin film layers fabrication scheme.	66
4.2	Porous membranes fabrication scheme. The multi-layer structure is foamed via physical foaming. Finally the porous membrane is suspended in water for further manipulations.	67
4.3	(a) Effect of the gas barrier scheme, bubble are only formed underneath the PVA barrier, as the blowing agent cannot escape from the film surfaces. (b) Evidence of the effect of the barrier, the presence of bubbles is evident from the color change of the film from transparent to white.	68
4.4	Picture of a free standing porous membrane suspended in diluted water.	69
4.5	SEM images of the cross section of a porous membrane. The cells are open on the bottom side, in contact with the PEDOT:PSS, while are not fully open on the top side.	70
4.6	SEM images of the top view of the porous membranes. Images of two different membranes produced at the same foaming condition, (a) upper closed cells, (b) open cells on both side of the film.	71
4.7	Porous membranes morphology details. (a) upper close cells with collapsing holes on the top side; (b) upper close cells with a rounded holes on the top side; (c) open cells with collapsed top walls with a typical shape resulting from coalescence; (d) open cells with a corrugated shaped lateral walls.	72
4.8	Microscope images of porous membranes produced (a) via pressure quench gas foaming, and (b) coarsening driven foaming procedure.	73
5.1	FASnI ₃ polymer compatibility test of the perovskite solution 0.8M with different concentration of both P2VP and P4VP. The solution results opaque for concentration of P4VP higher than 0.047 mg/mL, while there is evidence of visible formation of white particle for higher concentration.	80
5.2	Deposition process scheme, namely, dispersion dripping, spin coating and annealing of (a) the reference film, and with (b) P2VP 50mg/mL, (c) P2VP 100 mg/mL. Effect of P2VP on the crystallization process is highlighted from the color transition of the film from yellow to red to black.	81

5.3	Picture of the film after the deposition process. Reference film appears grey and opaque (left), P2VP 50 mg/mL is black and opaque (center), P2VP 100 mg/mL is black and lucid (right).	82
5.4	Perovskite film thickness analysis. (a) SEM images of the cross section of perovskite films with different polymer concentration; (b) effect of the overall polymer concentration on the film thickness at different $n_{\text{pyridine}}/n_{\text{Sn}}$ ratio, ranging from 0.36 tp 1.19.	83
5.5	XRD patterns of the FASnI_3 and FASnI_3 -P2VP perovskite composite film with different concentration of polymer added in the precursor dispersion (0.8 M), namely, 1, 10, 50, and 100 mg/mL. (* marked peaks are referred to the ITO) . . .	84
5.6	Peak intensity ratio, namely $I_{(100)}/I_{(120)}$ of perovskite (0.8 M) films treated with different P2VP concentrations (1, 10, 50, and 100 mg/mL).	85
5.7	SEM images of the top view of the perovskite films of the reference film (FASnI_3) and with different amount a of P2VP added in a 0.8 M precursors dispersion.	86
5.8	Morphology characterization of the perovskite P2VP composite film. (a) SEM of the cross section P2VP 50 mg/mL ($n_{\text{pyridine}}/n_{\text{Sn}} = 0.58$). (b) Morphology model representation.	87
5.9	J-V curves of PSCs based on FASnI_3 with tBP and a mixture of P2VP+tBP and P4VP+tBP. The device are tested both in forward (FS) and reverse (RS) scan direction.	88
5.10	Characteristics photovoltaic performance parameters, namely (a) short circuit current density (J_{sc}), (b) open circuit voltage (V_{oc}), (c) fill factor (FF), and (d) Power conversion efficiency (PCE) for FASnI_3 0.8 M based device processed with tBP, a mixture of P2VP+tBP, and P4VP+tBP. The plot highlights the distribution and variability of each property, providing insight into the impact of different additives on device efficiency and performance.	89
A.1	G' , G'' , and viscosity (η) of polypropylene (PP) as a function of the shear rate.	97

B.1	Spin coating parameter optimization in static mode	100
B.2	Spin coating parameter optimization in dynamic mode	101
B.3	Thickness measurement of PLGA film deposited via spin coating	102

Bibliography

- [1] Ernesto Di Maio, Salvatore Iannace, and Giuseppe Mensitieri. *Foaming with Supercritical Fluids*. Elsevier, 2021.
- [2] Yong-Biao Yang, Wenqiang Chai, Liang Zhang, Jiayao Wang, and Jichun You. A mini-review of polymeric porous membranes with vertically penetrative pores. *Journal of Polymer Science*, 62(3):492–507, 2024.
- [3] He Dong, Chenxin Ran, Weiyin Gao, Nan Sun, Xin Liu, Yingdong Xia, Yonghua Chen, and Wei Huang. Crystallization dynamics of sn-based perovskite thin films: toward efficient and stable photovoltaic devices. *Advanced Energy Materials*, 12(1):2102213, 2022.
- [4] John L West. Phase separation of liquid crystals in polymers. *Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics*, 157(1):427–441, 1988.
- [5] Brian L Cushing, Vladimir L Kolesnichenko, and Charles J O’connor. Recent advances in the liquid-phase syntheses of inorganic nanoparticles. *Chemical reviews*, 104(9):3893–3946, 2004.
- [6] Julius Frenkel. A general theory of heterophase fluctuations and pretransition phenomena. *The Journal of Chemical Physics*, 7(7):538–547, 1939.

-
- [7] David W Oxtoby. Nucleation of first-order phase transitions. *Accounts of chemical research*, 31(2):91–97, 1998.
- [8] Victor K La Mer. Nucleation in phase transitions. *Industrial & Engineering Chemistry*, 44(6):1270–1277, 1952.
- [9] James J De Yoreo, Pupa UPA Gilbert, Nico AJM Somerdijk, R Lee Penn, Stephen Whitelam, Derk Joester, Hengzhong Zhang, Jeffrey D Rimer, Alexandra Navrotsky, Jilian F Banfield, et al. Crystallization by particle attachment in synthetic, biogenic, and geologic environments. *Science*, 349(6247):aaa6760, 2015.
- [10] A_K Chesters. Modelling of coalescence processes in fluid-liquid dispersions: a review of current understanding. *Chemical engineering research and design*, 69(A4):259–270, 1991.
- [11] Peter W Voorhees. The theory of ostwald ripening. *Journal of Statistical Physics*, 38:231–252, 1985.
- [12] Carl Wagner. Theorie der alterung von niederschlägen durch umlösen (ostwald-reifung). *Zeitschrift für Elektrochemie, Berichte der Bunsengesellschaft für physikalische Chemie*, 65(7-8):581–591, 1961.
- [13] Daniele Tammaro and Ernesto Di Maio. Early bubble coalescence in thermoplastic foaming. *Materials Letters*, 228:459–462, 2018.
- [14] Brent S Murray and Rammile Ettelaie. Foam stability: proteins and nanoparticles. *Current opinion in colloid & interface science*, 9(5):314–320, 2004.
- [15] Lan Wang, Guilin Liu, Xi Xi, Guofeng Yang, Lifa Hu, Bingjie Zhu, Yifeng He, Yushen Liu, Hongqiang Qian, Shude Zhang, et al. Annealing engineering in the growth of perovskite grains. *Crystals*, 12(7):894, 2022.
-

-
- [16] James J De Yoreo and Peter G Vekilov. Principles of crystal nucleation and growth. *Reviews in mineralogy and geochemistry*, 54(1):57–93, 2003.
- [17] Yan Wang, Huixiang Zhang, Lun Cai, Fumin Xue, Hui Chen, Junbo Gong, and Shichao Du. Polymer-mediated and ultrasound-assisted crystallization of ropivacaine: Crystal growth and morphology modulation. *Ultrasonics Sonochemistry*, 97:106475, 2023.
- [18] Ke-Jun Wu, CM Edmund, Congxiao Shang, and Zhengxiao Guo. Nucleation and growth in solution synthesis of nanostructures—from fundamentals to advanced applications. *Progress in Materials Science*, 123:100821, 2022.
- [19] Joseph A Sarver and Erdogan Kiran. Foaming of polymers with carbon dioxide—the year-in-review—2019. *The Journal of Supercritical Fluids*, 173:105166, 2021.
- [20] Wentao Zhai, Junjie Jiang, and Chul B Park. A review on physical foaming of thermoplastic and vulcanized elastomers. *Polymer Reviews*, 62(1):95–141, 2022.
- [21] Daniel Raps, Nemat Hossieny, Chul B Park, and Volker Altstädt. Past and present developments in polymer bead foams and bead foaming technology. *Polymer*, 56:5–19, 2015.
- [22] Chul B Park, Amir H Behraves, and Ronald D Venter. Low density microcellular foam processing in extrusion using co₂. *Polymer Engineering & Science*, 38(11):1812–1823, 1998.
- [23] Andrzej Kornelius Bledzki, Hendrik Kirschling, Martin Rohleder, and Andris Chate. Correlation between injection moulding processing parameters and mechanical properties of microcellular polycarbonate. *Journal of Cellular Plastics*, 48(4):301–340, 2012.
- [24] Chengbiao Ge, Qian Ren, Shiping Wang, Wenge Zheng, Wentao Zhai, and Chul B Park. Steam-chest molding of expanded
-

- thermoplastic polyurethane bead foams and their mechanical properties. *Chemical Engineering Science*, 174:337–346, 2017.
- [25] D Tammaro, V Contaldi, Maria Giovanna Pastore Carbone, E Di Maio, and S Iannace. A novel lab-scale batch foaming equipment: The mini-batch. *Journal of Cellular Plastics*, 52(5):533–543, 2016.
- [26] Kentaro Taki, Takashi Nakayama, Taichi Yatsuzuka, and Masahiro Ohshima. Visual observations of batch and continuous foaming processes. *Journal of Cellular Plastics*, 39(2):155–169, 2003.
- [27] Ernesto Di Maio, Giuseppe Mensitieri, S Iannace, L Nicolais, W Li, and RW Flumerfelt. Structure optimization of polycaprolactone foams by using mixtures of co₂ and n₂ as blowing agents. *Polymer Engineering & Science*, 45(3):432–441, 2005.
- [28] James J Feng and Christopher A Bertelo. Prediction of bubble growth and size distribution in polymer foaming based on a new heterogeneous nucleation model. *Journal of Rheology*, 48(2):439–462, 2004.
- [29] Kentaro Taki, Kazuhide Tabata, Shin-Ichi Kihara, and Masahiro Ohshima. Bubble coalescence in foaming process of polymers. *Polymer Engineering & Science*, 46(5):680–690, 2006.
- [30] Kentaro Taki. Experimental and numerical studies on the effects of pressure release rate on number density of bubbles and bubble growth in a polymeric foaming process. *Chemical Engineering Science*, 63(14):3643–3653, 2008.
- [31] NS Ramesh, Don H Rasmussen, and Gregory A Campbell. Numerical and experimental studies of bubble growth during the microcellular foaming process. *Polymer Engineering & Science*, 31(23):1657–1664, 1991.
-

-
- [32] David C Venerus, N Yala, and B Bernstein. Analysis of diffusion-induced bubble growth in viscoelastic liquids. *Journal of Non-Newtonian Fluid Mechanics*, 75(1):55–75, 1998.
- [33] Chul B Park, Daniel F Baldwin, and Nam P Suh. Effect of the pressure drop rate on cell nucleation in continuous processing of microcellular polymers. *Polymer Engineering & Science*, 35(5):432–440, 1995.
- [34] Xiaohua Liu and Peter X Ma. Polymeric scaffolds for bone tissue engineering. *Annals of biomedical engineering*, 32:477–486, 2004.
- [35] Daniele Di Mascolo, Anna Lisa Palange, Rosita Primavera, Francesca Macchi, Tiziano Catelani, Federica Piccardi, Raffaele Spanò, Miguel Ferreira, Roberto Marotta, Andrea Armirotti, et al. Conformable hierarchically engineered polymeric micromeshes enabling combinatorial therapies in brain tumours. *Nature Nanotechnology*, 16(7):820–829, 2021.
- [36] S-K Lee, G-R Yi, Jun Hyuk Moon, S-M Yang, and David J Pine. Pixellated photonic crystal films by selective photopolymerization. *Advanced Materials*, 18(16):2111–2116, 2006.
- [37] Ji Sun Park, Sun Hwa Lee, Tae Hee Han, and Sang Ouk Kim. Hierarchically ordered polymer films by templated organization of aqueous droplets. *Advanced functional materials*, 17(14):2315–2320, 2007.
- [38] Baohui Zhao, Jian Zhang, Xudong Wang, and Chenxi Li. Water-assisted fabrication of honeycomb structure porous film from poly (l-lactide). *Journal of Materials Chemistry*, 16(5):509–513, 2006.
- [39] Lorna J Gibson. Cellular solids. *Mrs Bulletin*, 28(4):270–274, 2003.
- [40] Daniele Tammaro, Antonello Astarita, Ernesto Di Maio, and Salvatore Iannace. Polystyrene foaming at high pressure
-

- drop rates. *Industrial & Engineering Chemistry Research*, 55(19):5696–5701, 2016.
- [41] Ruosong Li, Jung Hyub Lee, Chongda Wang, Lun Howe Mark, and Chul B Park. Solubility and diffusivity of CO_2 and N_2 in tpu and their effects on cell nucleation in batch foaming. *The Journal of Supercritical Fluids*, 154:104623, 2019.
- [42] Mostafa Salehi, Mostafa Rezaei, and Mahdi Salami Hosseini. Experimental and theoretical investigation on polystyrene/n-pentane foaming process. *International Journal of Material Forming*, 10:421–434, 2017.
- [43] Louis E Daigneault and Richard Gendron. Blends of CO_2 and 2-ethyl hexanol as replacement foaming agents for extruded polystyrene. *Journal of cellular plastics*, 37(3):262–272, 2001.
- [44] Yang Chen, Chenglong Weng, Zhen Wang, Tim Maertens, Ping Fan, Feng Chen, Mingqiang Zhong, Jun Tan, and Jintao Yang. Preparation of polymeric foams with bimodal cell size: An application of heterogeneous nucleation effect of nanofillers. *The Journal of Supercritical Fluids*, 147:107–115, 2019.
- [45] Zhonglei Ma, Guangcheng Zhang, Quan Yang, Xuetao Shi, and Aihua Shi. Fabrication of microcellular polycarbonate foams with unimodal or bimodal cell-size distributions using supercritical carbon dioxide as a blowing agent. *Journal of Cellular Plastics*, 50(1):55–79, 2014.
- [46] Marco Trofa, Ernesto Di Maio, and Pier Luca Maffettone. Multi-graded foams upon time-dependent exposition to blowing agent. *Chemical Engineering Journal*, 362:812–817, 2019.
- [47] Fabrizio Errichiello, Aniello Cammarano, Ernesto Di Maio, and Luigi Nicolais. Sintering graded foamed beads: Compressive properties. *Journal of Applied Polymer Science*, 139(18):52052, 2022.
-

-
- [48] Paolo Iaccarino, Elvira Maresca, Simone Morganti, Ferdinando Auricchio, and Ernesto Di Maio. Topologically optimized graded foams. *Advanced Engineering Materials*, 26(11):2301798, 2024.
- [49] Chengbiao Ge, Shiping Wang, Wenge Zheng, and Wentao Zhai. Preparation of microcellular thermoplastic polyurethane (tpu) foam and its tensile property. *Polymer Engineering & Science*, 58(S1):E158–E166, 2018.
- [50] Junjie Jiang, Hao Zheng, Huawen Liu, and Wentao Zhai. Tunable cell structure and mechanism in porous thermoplastic polyurethane micro-film fabricated by a diffusion-restricted physical foaming process. *The Journal of Supercritical Fluids*, 171:105205, 2021.
- [51] Lei Li, Hideaki Yokoyama, Taichi Nemoto, and Kenji Sugiyama. Facile fabrication of nanocellular block copolymer thin films using supercritical carbon dioxide. *Advanced materials*, 16(14):1226–1229, 2004.
- [52] Srinivas Siripurapu, Joseph M DeSimone, Saad A Khan, and Richard J Spontak. Low-temperature, surface-mediated foaming of polymer films. *Advanced Materials*, 16(12):989–994, 2004.
- [53] Silvia Orsi, Ernesto Di Maio, Salvatore Iannace, and Paolo A Netti. Hollow micro-and nano-particles by gas foaming. *Nano Research*, 7:1018–1026, 2014.
- [54] Michael Saliba, Juan-Pablo Correa-Baena, Michael Grätzel, Anders Hagfeldt, and Antonio Abate. Perovskite solar cells: from the atomic level to film quality and device performance. *Angewandte Chemie International Edition*, 57(10):2554–2569, 2018.
- [55] Nam-Gyu Park. Perovskite solar cells: an emerging photovoltaic technology. *Materials today*, 18(2):65–72, 2015.
-

-
- [56] Azhar Fakharuddin, Mahesh K Gangishetty, Mojtaba Abdi-Jalebi, Sang-Hyun Chin, Abd Rashid bin Mohd Yusoff, Daniel N Congreve, Wolfgang Tress, Felix Deschler, Maria Vasilopoulou, and Henk J Bolink. Perovskite light-emitting diodes. *Nature Electronics*, 5(4):203–216, 2022.
- [57] Cherie R Kagan, David B Mitzi, and Christos D Dimitrakopoulos. Organic-inorganic hybrid materials as semiconducting channels in thin-film field-effect transistors. *Science*, 286(5441):945–947, 1999.
- [58] Sandip Maiti, Sumanta Kumar Karan, Jin Kon Kim, and Bhanu Bhusan Khatua. Nature driven biopiezoelectric/triboelectric nanogenerator as next-generation green energy harvester for smart and pollution free society. *Advanced Energy Materials*, 9(9):1803027, 2019.
- [59] G Li, F Gunkel, J Wang, CB Park, and Volker Altstädt. Solubility measurements of n₂ and co₂ in polypropylene and ethene/octene copolymer. *Journal of applied polymer science*, 103(5):2945–2953, 2007.
- [60] Shuxia Tao, Ines Schmidt, Geert Brocks, Junke Jiang, Ionut Tranca, Klaus Meerholz, and Selina Olthof. Absolute energy level positions in tin-and lead-based halide perovskites. *Nature communications*, 10(1):2560, 2019.
- [61] Gary Hodes. Perovskite-based solar cells. *Science*, 342(6156):317–318, 2013.
- [62] NREL. Best research-cell efficiencies chart. <https://www.nrel.gov/pv/assets/images/es/efficiency-chart.jpg>, 2024. Accessed: 17 October 2024.
- [63] Junming Li, Hai-Lei Cao, Wen-Bin Jiao, Qiong Wang, Mingdeng Wei, Irene Cantone, Jian Lü, and Antonio Abate. Biological impact of lead from halide perovskites reveals the risk of introducing a safe threshold. *Nature communications*, 11(1):310, 2020.
-

-
- [64] Antonio Abate. Perovskite solar cells go lead free. *Joule*, 1(4):659–664, 2017.
- [65] Mahmoud Aldamasy, Zafar Iqbal, Guixiang Li, Jorge Pascual, Fahad Alharthi, Antonio Abate, and Meng Li. Challenges in tin perovskite solar cells. *Physical Chemistry Chemical Physics*, 23(41):23413–23427, 2021.
- [66] Luis Lanzetta, Thomas Webb, Nourdine Zibouche, Xinxing Liang, Dong Ding, Ganghong Min, Robert JE Westbrook, Benedetta Gaggio, Thomas J Macdonald, M Saiful Islam, et al. Degradation mechanism of hybrid tin-based perovskite solar cells and the critical role of tin (iv) iodide. *Nature communications*, 12(1):2853, 2021.
- [67] Zhihao Zhang, Yuanfang Huang, Jialun Jin, Yiting Jiang, Yuliang Xu, Jingwei Zhu, and Dewei Zhao. Mechanistic understanding of oxidation of tin-based perovskite solar cells and mitigation strategies. *Angewandte Chemie*, 135(45):e202308093, 2023.
- [68] Xin Zhang, Shurong Wang, Weike Zhu, Zhiyuan Cao, Aili Wang, and Feng Hao. The voltage loss in tin halide perovskite solar cells: origins and perspectives. *Advanced Functional Materials*, 32(8):2108832, 2022.
- [69] Alexander Sharenko and Michael F Toney. Relationships between lead halide perovskite thin-film fabrication, morphology, and performance in solar cells. *Journal of the American Chemical Society*, 138(2):463–470, 2016.
- [70] Lingling Zheng, Danfei Zhang, Yingzhuang Ma, Zelin Lu, Zhi-jian Chen, Shufeng Wang, Lixin Xiao, and Qihuang Gong. Morphology control of the perovskite films for efficient solar cells. *Dalton transactions*, 44(23):10582–10593, 2015.
- [71] Yutian Lei, Youkui Xu, Meng Wang, Ge Zhu, and Zhiwen Jin. Origin, influence, and countermeasures of defects in perovskite solar cells. *Small*, 17(26):2005495, 2021.
-

-
- [72] Yana Vaynzof. The future of perovskite photovoltaics—thermal evaporation or solution processing? *Advanced Energy Materials*, 10(48):2003073, 2020.
- [73] Fu Yang, Dongju Jang, Lirong Dong, Shudi Qiu, Andreas Disler, Ning Li, Christoph J Brabec, and Hans-Joachim Egelhaaf. Upscaling solution-processed perovskite photovoltaics. *Advanced energy materials*, 11(42):2101973, 2021.
- [74] Zhuojia Lin, Yang Su, Runying Dai, Gengling Liu, Jia Yang, Wangping Sheng, Yang Zhong, Licheng Tan, and Yiwang Chen. Ionic liquid-induced ostwald ripening effect for efficient and stable tin-based perovskite solar cells. *ACS Applied Materials & Interfaces*, 13(13):15420–15428, 2021.
- [75] Victor K LaMer and Robert H Dinegar. Theory, production and mechanism of formation of monodispersed hydrosols. *Journal of the american chemical society*, 72(11):4847–4854, 1950.
- [76] Minsu Jung, Sang-Geun Ji, Gwisu Kim, and Sang Il Seok. Perovskite precursor solution chemistry: from fundamentals to photovoltaic applications. *Chemical Society Reviews*, 48(7):2011–2038, 2019.
- [77] Davide Amoroso, Giuseppe Nasti, Carolin M Sutter-Fella, Massimiliano M Villone, Pier Luca Maffettone, and Antonio Abate. The central role of colloids to explain the crystallization dynamics of halide perovskites: A critical review. *Matter*, 2024.
- [78] Marion A Flatken, Armin Hoell, Robert Wendt, Eneli Härk, André Dallmann, Albert Prause, Jorge Pascual, Eva Unger, and Antonio Abate. Small-angle scattering to reveal the colloidal nature of halide perovskite precursor solutions. *Journal of Materials Chemistry A*, 9(23):13477–13482, 2021.
- [79] Marion A Flatken, Eros Radicchi, Robert Wendt, Ana Guilherme Buzanich, Eneli Hark, Jorge Pascual, Florian Mathies, Oleksandra Shargaieva, Albert Prause, André Dallmann, et al.
-

- Role of the alkali metal cation in the early stages of crystallization of halide perovskites. *Chemistry of Materials*, 34(3):1121–1131, 2022.
- [80] Yao Zhang, Chunyan Li, Haiyan Zhao, Zhongxun Yu, Xiaolan Tang, Jixiang Zhang, Zhenhua Chen, Jianrong Zeng, Peng Zhang, Liyuan Han, et al. Synchronized crystallization in tin-lead perovskite solar cells. *Nature communications*, 15(1):6887, 2024.
- [81] Jorge Pascual, Giuseppe Nasti, Mahmoud H Aldamasy, Joel A Smith, Marion Flatken, Nga Phung, Diego Di Girolamo, Silver-Hamill Turren-Cruz, Meng Li, André Dallmann, et al. Origin of sn (ii) oxidation in tin halide perovskites. *Materials Advances*, 1(5):1066–1070, 2020.
- [82] Diego Di Girolamo, Jorge Pascual, Mahmoud H Aldamasy, Zafar Iqbal, Guixiang Li, Eros Radicchi, Meng Li, Silver-Hamill Turren-Cruz, Giuseppe Nasti, Andre Dallmann, et al. Solvents for processing stable tin halide perovskites. *ACS Energy Letters*, 6(3):959–968, 2021.
- [83] Enrico Della Gaspera, Yong Peng, Qicheng Hou, Leone Spiccia, Udo Bach, Jacek J Jasieniak, and Yi-Bing Cheng. Ultra-thin high efficiency semitransparent perovskite solar cells. *Nano Energy*, 13:249–257, 2015.
- [84] Zengqi Huang, Xiaotian Hu, Cong Liu, Licheng Tan, and Yiwang Chen. Nucleation and crystallization control via polyurethane to enhance the bendability of perovskite solar cells with excellent device performance. *Advanced Functional Materials*, 27(41):1703061, 2017.
- [85] Jiewei Liu, Masashi Ozaki, Shinya Yakumaru, Taketo Handa, Ryosuke Nishikubo, Yoshihiko Kanemitsu, Akinori Saeki, Yasujiro Murata, Richard Murdey, and Atsushi Wakamiya. Lead-free solar cells based on tin halide perovskite films with high
-

- coverage and improved aggregation. *Angewandte Chemie*, 130(40):13405–13409, 2018.
- [86] Chuantian Zuo and Liming Ding. An 80.11% ff record achieved for perovskite solar cells by using the nh 4 cl additive. *Nanoscale*, 6(17):9935–9938, 2014.
- [87] Min Xiao, Shuai Gu, Pengchen Zhu, Mingyao Tang, Weidong Zhu, Renxing Lin, Chuanlu Chen, Weichao Xu, Tao Yu, and Jia Zhu. Tin-based perovskite with improved coverage and crystallinity through tin-fluoride-assisted heterogeneous nucleation. *Advanced Optical Materials*, 6(1):1700615, 2018.
- [88] Fei Wang, Xianyuan Jiang, Hao Chen, Yuequn Shang, Hefei Liu, Jingle Wei, Wenjia Zhou, Hailong He, Weimin Liu, and Zhijun Ning. 2d-quasi-2d-3d hierarchy structure for tin perovskite solar cells with enhanced efficiency and stability. *Joule*, 2(12):2732–2743, 2018.
- [89] Liangliang Deng, Kai Wang, Hanjun Yang, Haomiao Yu, and Bin Hu. Polymer assist crystallization and passivation for enhancements of open-circuit voltage and stability in tin-halide perovskite solar cells. *Journal of Physics D: Applied Physics*, 51(47):475102, 2018.
- [90] Gengling Liu, Cong Liu, Zhuojia Lin, Jia Yang, Zengqi Huang, Licheng Tan, and Yiwang Chen. Regulated crystallization of efficient and stable tin-based perovskite solar cells via a self-sealing polymer. *ACS applied materials & interfaces*, 12(12):14049–14056, 2020.
- [91] Xiangyue Meng, Jianbo Lin, Xiao Liu, Xin He, Yong Wang, Takeshi Noda, Tianhao Wu, Xudong Yang, and Liyuan Han. Highly stable and efficient fasni3-based perovskite solar cells by introducing hydrogen bonding. *Advanced Materials*, 31(42):1903721, 2019.
- [92] Junfang Wang, Chenglin Yang, Hao Chen, Mingsheng Lv, Tianhua Liu, Haining Chen, Ding-Jiang Xue, Jin-Song Hu,
-

- Liyuan Han, Shihe Yang, et al. Oriented attachment of tin halide perovskites for photovoltaic applications. *ACS Energy Letters*, 8(3):1590–1596, 2023.
- [93] Danyu Cui, Xiao Liu, Tianhao Wu, Xuesong Lin, Xinhui Luo, Yongzhen Wu, Hiroshi Segawa, Xudong Yang, Yiqiang Zhang, Yanbo Wang, et al. Making room for growing oriented fasni₃ with large grains via cold precursor solution. *Advanced Functional Materials*, 31(25):2100931, 2021.
- [94] Brian L Watson, Nicholas Rolston, Adam D Printz, and Reinhold H Dauskardt. Scaffold-reinforced perovskite compound solar cells. *Energy & Environmental Science*, 10(12):2500–2508, 2017.
- [95] Woongchan Lee, Young Jin Yoo, Jinhong Park, Joo Hwan Ko, Yeong Jae Kim, Huiwon Yun, Dong Hoe Kim, Young Min Song, and Dae-Hyeong Kim. Perovskite microcells fabricated using swelling-induced crack propagation for colored solar windows. *Nature communications*, 13(1):1946, 2022.
- [96] Wenjia Li, Bei Cheng, Peng Xiao, Tao Chen, Jianjun Zhang, and Jiaguo Yu. Low-temperature-processed monolayer inverse opal sno₂ scaffold for efficient perovskite solar cells. *Small*, 18(49):2205097, 2022.
- [97] John W Boretos and William S Pierce. Segmented polyurethane: a new elastomer for biomedical applications. *Science*, 158(3807):1481–1482, 1967.
- [98] Bin Lan, Pengzhi Li, Qi Yang, and Pengjian Gong. Dynamic self generation of hydrogen bonding and relaxation of polymer chain segment in stabilizing thermoplastic polyurethane micro-cellular foams. *Materials Today Communications*, 24:101056, 2020.
- [99] Achim Frick and Arif Rochman. Characterization of tpu-elastomers by thermal analysis (dsc). *Polymer testing*, 23(4):413–417, 2004.
-

-
- [100] Geoffrey Holden. Thermoplastic elastomers. In *Applied plastics engineering handbook*, pages 77–91. Elsevier, 2011.
- [101] Guilong Wang, Gengping Wan, Jialong Chai, Bo Li, Guoqun Zhao, Yue Mu, and Chul B Park. Structure-tunable thermoplastic polyurethane foams fabricated by supercritical carbon dioxide foaming and their compressive mechanical properties. *The Journal of Supercritical Fluids*, 149:127–137, 2019.
- [102] EM Christenson, JM Anderson, and A Hiltner. Biodegradation mechanisms of polyurethane elastomers. *Corrosion Engineering, Science and Technology*, 42(4):312–323, 2007.
- [103] Mohammad Faisal Ahmed, Yan Li, Zhen Yao, Kun Cao, and Changchun Zeng. Tpu/pla blend foams: Enhanced foamability, structural stability, and implications for shape memory foams. *Journal of Applied Polymer Science*, 136(17):47416, 2019.
- [104] Piotr Krol. Synthesis methods, chemical structures and phase structures of linear polyurethanes. properties and applications of linear polyurethanes in polyurethane elastomers, copolymers and ionomers. *Progress in materials science*, 52(6):915–1015, 2007.
- [105] Murat Ates, Selin Karadag, Aysegul Akdogan Eker, and Bulent Eker. Polyurethane foam materials and their industrial applications. *Polymer International*, 71(10):1157–1163, 2022.
- [106] Hrishikesh A Kharbas, Jason D McNulty, Thomas Ellingham, Cyrus Thompson, Mihai Manitiu, Guenter Scholz, and Lih-Sheng Turng. Comparative study of chemical and physical foaming methods for injection-molded thermoplastic polyurethane. *Journal of Cellular Plastics*, 53(4):373–388, 2017.
- [107] Martial Sauceau, Jacques Fages, Audrey Common, Clémence Nikitine, and Elisabeth Rodier. New challenges in polymer
-

- foaming: A review of extrusion processes assisted by supercritical carbon dioxide. *Progress in Polymer Science*, 36(6):749–766, 2011.
- [108] Kentaro Taki, Daisaku Kitano, and Masahiro Ohshima. Effect of growing crystalline phase on bubble nucleation in poly (l-lactide)/co2 batch foaming. *Industrial & Engineering Chemistry Research*, 50(6):3247–3252, 2011.
- [109] Zhihua Guo, Adam C Burley, Kurt W Koelling, Isamu Kusaka, L James Lee, and David L Tomasko. Co2 bubble nucleation in polystyrene: Experimental and modeling studies. *Journal of Applied Polymer Science*, 125(3):2170–2186, 2012.
- [110] Nemat J Hossieny, Mohamad Reza Barzegari, Mohammadreza Nofar, Syed H Mahmood, and Chul B Park. Crystallization of hard segment domains with the presence of butane for microcellular thermoplastic polyurethane foams. *Polymer*, 55(2):651–662, 2014.
- [111] Richard Gendron, Michel F Champagne, Yadi Delaviz, and Mark E Polasky. Foaming polystyrene with a mixture of co2 and ethanol. *Journal of cellular plastics*, 42(2):127–138, 2006.
- [112] Aurelio Salerno, Ugo Clerici, and Concepción Domingo. Solid-state foaming of biodegradable polyesters by means of supercritical co2/ethyl lactate mixtures: Towards designing advanced materials by means of sustainable processes. *European polymer journal*, 51:1–11, 2014.
- [113] Ioannis Tsivintzelis, Eleni Pavlidou, and Costas Panayiotou. Biodegradable polymer foams prepared with supercritical co2–ethanol mixtures as blowing agents. *The Journal of supercritical fluids*, 42(2):265–272, 2007.
- [114] Na Zhao, Lun Howe Mark, Changwei Zhu, Chul B Park, Qian Li, Robert Glenn, and Todd Ryan Thompson. Foaming poly (vinyl alcohol)/microfibrillated cellulose composites with co2
-

- and water as co-blowing agents. *Industrial & Engineering Chemistry Research*, 53(30):11962–11972, 2014.
- [115] Cailiang Zhang, Bin Zhu, and L James Lee. Extrusion foaming of polystyrene/carbon particles using carbon dioxide and water as co-blowing agents. *Polymer*, 52(8):1847–1855, 2011.
- [116] Heinz Voelker, Gerhard Alicke, Horst Schuch, Manfred Weilbacher, and Reinhold Weber. Production of foam sheets of high compressive strength, January 26 1993. US Patent 5,182,308.
- [117] Andra Nistor, Adam Rygl, Marek Bobak, Marie Sajfirtova, and Juraj Kosek. Micro-cellular polystyrene foam preparation using high pressure co₂: The influence of solvent residua. In *Macromolecular Symposia*, volume 333, pages 266–272. Wiley Online Library, 2013.
- [118] Andra Nistor, Martin Topiar, Helena Sovova, and Juraj Kosek. Effect of organic co-blowing agents on the morphology of co₂ blown microcellular polystyrene foams. *The Journal of Supercritical Fluids*, 130:30–39, 2017.
- [119] Xiaoqin Lan, Wentao Zhai, and Wenge Zheng. Critical effects of polyethylene addition on the autoclave foaming behavior of polypropylene and the melting behavior of polypropylene foams blown with n-pentane and co₂. *Industrial & Engineering Chemistry Research*, 52(16):5655–5665, 2013.
- [120] TR Tuladhar and MR Mackley. Experimental observations and modelling relating to foaming and bubble growth from pentane loaded polystyrene melts. *Chemical Engineering Science*, 59(24):5997–6014, 2004.
- [121] Gabriela Salejova and Juraj Kosek. Dynamics of foaming of polystyrene particles. In *Macromolecular Symposia*, volume 243, pages 233–246. Wiley Online Library, 2006.
- [122] Hamid Reza Azimi, Mostafa Rezaei, and Farhang Abbasi. The effect of expansion conditions on the batch foaming dynamics
-

- of st-mma copolymer. *Journal of Cellular Plastics*, 48(2):125–140, 2012.
- [123] Hamid Reza Azimi, Mostafa Rezaei, and Mostafa Salehi. The effect of copolymer composition on the batch foaming dynamics of styrene/methylmethacrylate copolymers. *Journal of Thermoplastic Composite Materials*, 30(1):47–66, 2017.
- [124] Shu Kai Yeh, Ying Ru Chen, Ting Wei Kang, Tzu Jian Tseng, Sheng Ping Peng, Chien Chia Chu, Syang Peng Rwei, and Wen Jeng Guo. Different approaches for creating nanocellular tpu foams by supercritical co2 foaming. *Journal of Polymer Research*, 25:1–12, 2018.
- [125] Lambiotte & Cie. Products, Methyal, 2023. <https://www.lambiotte.com/methyal/>, last accessed on 2023-09-25.
- [126] Ruiyan Sun, Irina Delidovich, and Regina Palkovits. Dimethoxymethane as a cleaner synthetic fuel: synthetic methods, catalysts, and reaction mechanism. *ACS Catalysis*, 9(2):1298–1318, 2019.
- [127] Leszek Wianowski, Anita Białkowska, Lucjan Dobrowolski, and Iwona Zarzyka. Physical blowing agents for polyurethanes. *Polimery*, 65(2):83–94, 2020.
- [128] Maria Kurańska, Aleksander Prociak, Sławomir Michałowski, and A Zawadzińska. The influence of blowing agents type on foaming process and properties of rigid polyurethane foams. *Polimery*, 63 (2018) 672-678, 2018.
- [129] Yichong Chen, Dongyang Li, Hong Zhang, Yijie Ling, Kaiwen Wu, Tao Liu, Dongdong Hu, and Ling Zhao. Antishrinking strategy of microcellular thermoplastic polyurethane by comprehensive modeling analysis. *Industrial & Engineering Chemistry Research*, 60(19):7155–7166, 2021.
-

-
- [130] Xiulu Gao, Yichong Chen, Peng Chen, Zhimei Xu, Ling Zhao, and Dongdong Hu. Supercritical co₂ foaming and shrinkage resistance of thermoplastic polyurethane/modified magnesium borate whisker composite. *Journal of CO₂ Utilization*, 57:101887, 2022.
- [131] Daniele Tammaro, Attilio De Maio, Maria Giovanna Pastore Carbone, Ernesto Di Maio, and Salvatore Iannace. Ps foams at high pressure drop rates. In *AIP Conference Proceedings*, volume 1599, pages 473–476. American Institute of Physics, 2014.
- [132] Michael Albert, Immanuel Hahnenstein, Hans Hasse, and Gerd Maurer. Vapor- liquid and liquid- liquid equilibria in binary and ternary mixtures of water, methanol, and methylal. *Journal of Chemical & Engineering Data*, 46(4):897–903, 2001.
- [133] Kenneth A Kobe and Joseph F Mathews. Critical properties and vapor pressures of some organic nitrogen and oxygen compounds. *Journal of Chemical and Engineering Data*, 15(1):182–186, 1970.
- [134] Jiawei Lu, Hong Zhang, Yuemiao Chen, Yukai Ge, and Tao Liu. Effect of chain relaxation on the shrinkage behavior of tpee foams fabricated with supercritical co₂. *Polymer*, 256:125262, 2022.
- [135] Caroline A Schneider, Wayne S Rasband, and Kevin W Elceiri. Nih image to imagej: 25 years of image analysis. *Nature methods*, 9(7):671–675, 2012.
- [136] Cosimo Brondi, Maria Rosaria Di Caprio, Giuseppe Scherillo, Ernesto Di Maio, Thomas Mosciatti, Sara Cavalca, Vanni Parenti, Maurizio Corti, and Salvatore Iannace. Thermosetting polyurethane foams by physical blowing agents: Chasing the synthesis reaction with the pressure. *The Journal of Supercritical Fluids*, 154:104630, 2019.
-

-
- [137] Jin-Biao Bao, Tao Liu, Ling Zhao, and Guo-Hua Hu. A two-step depressurization batch process for the formation of bimodal cell structure polystyrene foams using scCO₂. *The Journal of Supercritical Fluids*, 55(3):1104–1114, 2011.
- [138] Daniele Tammaro, Gaetano D’Avino, Ernesto Di Maio, Rossana Pasquino, MM Villone, D Gonzales, M Groombridge, Nino Grizzuti, and PL Maffettone. Validated modeling of bubble growth, impingement and retraction to predict cell-opening in thermoplastic foaming. *Chemical Engineering Journal*, 287:492–502, 2016.
- [139] Li Jun, Ziwei Qin, Hao-Yang Mi, Bin-Bin Dong, Chuntai Liua, and Changyu Shena. Fabrication of thermoplastic polyurethane foams with wrinkled pores and superior energy absorption properties by CO₂ foaming and fast chilling. *Macromolecular Materials and Engineering*, 307(1):2100600, 2022.
- [140] Maria Giovanna Pastore Carbone, Ernesto Di Maio, Salvatore Iannace, and Giuseppe Mensitieri. Simultaneous experimental evaluation of solubility, diffusivity, interfacial tension and specific volume of polymer/gas solutions. *Polymer Testing*, 30(3):303–309, 2011.
- [141] Shweta Deotale, Sayantani Dutta, JA Moses, VM Balasubramaniam, and C Anandharamakrishnan. Foaming characteristics of beverages and its relevance to food processing. *Food Engineering Reviews*, 12:229–250, 2020.
- [142] Gaojian Wu, Pengcheng Xie, Huaguang Yang, Kaifang Dang, Yuxuan Xu, Mohini Sain, Lih-Sheng Turng, and Weimin Yang. A review of thermoplastic polymer foams for functional applications. *Journal of Materials Science*, 56:11579–11604, 2021.
- [143] Benjamin Dollet, Philippe Marmottant, and Valeria Garbin. Bubble dynamics in soft and biological matter. *Annual Review of Fluid Mechanics*, 51:331–355, 2019.
-

-
- [144] A Arefmanesh and SG Advani. Diffusion-induced growth of a gas bubble in a viscoelastic fluid. *Rheologica Acta*, 30:274–283, 1991.
- [145] Chang Dae Han and Hee Ju Yoo. Studies on structural foam processing. iv. bubble growth during mold filling. *Polymer Engineering & Science*, 21(9):518–533, 1981.
- [146] Mitsutaka Shimoda, Isao Tsujimura, Masataka Tanigaki, and Masahiro Ohshima. Polymeric foaming simulation for extrusion processes. *Journal of Cellular Plastics*, 37(6):517–536, 2001.
- [147] Jingkui Yang, Tuanhui Jiang, Bujin Liu, Chun Zhang, Xiangbu Zeng, Li He, and Wei Gong. Experimental and numerical analysis of bubble nucleation in foaming polymer. *Materials & Design*, 203:109577, 2021.
- [148] Qingping Guo, Jin Wang, Chul B Park, and Masahiro Ohshima. A microcellular foaming simulation system with a high pressure-drop rate. *Industrial & Engineering Chemistry Research*, 45(18):6153–6161, 2006.
- [149] Siu N Leung, Anson Wong, Lilac Cuiling Wang, and Chul B Park. Mechanism of extensional stress-induced cell formation in polymeric foaming processes with the presence of nucleating agents. *The Journal of Supercritical Fluids*, 63:187–198, 2012.
- [150] Siu N Leung, Chul B Park, Donglai Xu, Hongbo Li, and Robert G Fenton. Computer simulation of bubble-growth phenomena in foaming. *Industrial & engineering chemistry research*, 45(23):7823–7831, 2006.
- [151] Kentaro Taki, Marco Menale, Giovanni Pisante, and Ernesto Di Maio. A design tool for core-back timing in foam injection molding. *Journal of Applied Polymer Science*, 139(45):e53121, 2022.
- [152] Stefano Acierno and Nino Grizzuti. Measurements of the rheological behavior of a crystallizing polymer by an “inverse
-

- quenching” technique. *Journal of Rheology*, 47(2):563–576, 03 2003.
- [153] Takeshi Ishikawa, Kentaro Taki, and Masahiro Ohshima. Visual observation and numerical studies of n₂ vs. co₂ foaming behavior in core-back foam injection molding. *Polymer Engineering & Science*, 52(4):875–883, 2012.
- [154] RASBAND WS. Imagej, us national institutes of health, bethesda, maryland, usa. <http://imagej.nih.gov/ij/>, 2011.
- [155] V Talanquer and David W Oxtoby. Nucleation of bubbles in binary fluids. *The Journal of chemical physics*, 102(5):2156–2164, 1995.
- [156] Satish K Goel and Eric J Beckman. Generation of microcellular polymeric foams using supercritical carbon dioxide. i: Effect of pressure and temperature on nucleation. *Polymer Engineering & Science*, 34(14):1137–1147, 1994.
- [157] Ioannis Tsivintzelis, Anastasia G Angelopoulou, and Costas Panayiotou. Foaming of polymers with supercritical co₂: An experimental and theoretical study. *Polymer*, 48(20):5928–5939, 2007.
- [158] Daniel E Rosner and Michael Epstein. Effects of interface kinetics, capillarity and solute diffusion on bubble growth rates in highly supersaturated liquids. *Chemical Engineering Science*, 27(1):69–88, 1972.
- [159] MA Shafi and RW Flumerfelt. Initial bubble growth in polymer foam processes. *Chemical Engineering Science*, 52(4):627–633, 1997.
- [160] Brice Saint-Michel and Valeria Garbin. Bubble dynamics for broadband microrheology of complex fluids. *Current Opinion in Colloid & Interface Science*, 50:101392, 2020.
-

-
- [161] P Taylor. Ostwald ripening in emulsions. *Advances in colloid and interface science*, 75(2):107–163, 1998.
- [162] Ilya M Lifshitz and Vitaly V Slyozov. The kinetics of precipitation from supersaturated solid solutions. *Journal of physics and chemistry of solids*, 19(1-2):35–50, 1961.
- [163] Robert Lemlich. Prediction of changes in bubble size distribution due to interbubble gas diffusion in foam. *Industrial & Engineering Chemistry Fundamentals*, 17(2):89–93, 1978.
- [164] Robert I Saye and James A Sethian. Multiscale modeling of membrane rearrangement, drainage, and rupture in evolving foams. *Science*, 340(6133):720–724, 2013.
- [165] Robert D MacPherson and David J Srolovitz. The von neumann relation generalized to coarsening of three-dimensional microstructures. *Nature*, 446(7139):1053–1055, 2007.
- [166] James A Glazier and Denis Weaire. The kinetics of cellular patterns. *Journal of Physics: Condensed Matter*, 4(8):1867, 1992.
- [167] Paul S Epstein and Milton S Plesset. On the stability of gas bubbles in liquid-gas solutions. *The Journal of Chemical Physics*, 18(11):1505–1509, 1950.
- [168] P Brent Duncan and David Needham. Test of the epstein- plesset model for gas microparticle dissolution in aqueous media: effect of surface tension and gas undersaturation in solution. *Langmuir*, 20(7):2567–2578, 2004.
- [169] Poulichet Vincent and Garbin Valeria. Cooling particle-coated bubbles: Destabilization beyond dissolution arrest. 2015.
- [170] M Kontopoulou and John Vlachopoulos. Bubble dissolution in molten polymers and its role in rotational molding. *Polymer Engineering & Science*, 39(7):1189–1198, 1999.
-

-
- [171] Ying Sun, Yumi Ueda, Hiroyuki Suganaga, Masashi Haruki, Shin-ichi Kihara, and Shigeki Takishima. Pressure drop threshold in the foaming of low-density polyethylene, polystyrene, and polypropylene using co₂ and n₂ as foaming agents. *The Journal of Supercritical Fluids*, 103:38–47, 2015.
- [172] Preston L Durrill and Richard G Griskey. Diffusion and solution of gases in thermally softened or molten polymers: Part i. development of technique and determination of data. *AIChE Journal*, 12(6):1147–1151, 1966.
- [173] Gianluca Laghezza, Erik Dietrich, Julia M Yeomans, Rodrigo Ledesma-Aguilar, E Stefan Kooij, Harold JW Zandvliet, and Detlef Lohse. Collective and convective effects compete in patterns of dissolving surface droplets. *Soft matter*, 12(26):5787–5796, 2016.
- [174] Sébastien Michelin, Etienne Guérin, and Eric Lauga. Collective dissolution of microbubbles. *Physical Review Fluids*, 3(4):043601, 2018.
- [175] Joost H Weijs, James RT Seddon, and Detlef Lohse. Diffusive shielding stabilizes bulk nanobubble clusters. *ChemPhysChem*, 13(8):2197–2204, 2012.
- [176] Christopher Hill and Julian Eastoe. Foams: From nature to industry. *Advances in colloid and interface science*, 247:496–513, 2017.
- [177] Yukai Ge, Jiawei Lu, and Tao Liu. Analysis of bubble coalescence and determination of the bubble radius for long-chain branched poly (ethylene terephthalate) melt foaming with a pressure balanced bubble-growth model. *AIChE Journal*, 66(4):e16862, 2020.
- [178] Marcos Borrell and L Gary Leal. Viscous coalescence of expanding low-viscosity drops; the dueling drops experiment. *Journal of colloid and interface science*, 319(1):263–269, 2008.
-

-
- [179] Dominique Langevin. Coalescence in foams and emulsions: Similarities and differences. *Current Opinion in Colloid & Interface Science*, 44:23–31, 2019.
- [180] Daniele Tammaro, Rossana Pasquino, Massimiliano Maria Vilone, Gaetano D’Avino, Vincenzo Ferraro, Ernesto Di Maio, Antonio Langella, Nino Grizzuti, and Pier Luca Maffettone. Elasticity in bubble rupture. *Langmuir*, 34(19):5646–5654, 2018.
- [181] Christopher R Anthony, Pritish M Kamat, Sumeet S Thete, James P Munro, John R Lister, Michael T Harris, and Osman A Basaran. Scaling laws and dynamics of bubble coalescence. *Physical Review Fluids*, 2(8):083601, 2017.
- [182] Alexandros T Oratis, Vincent Bertin, and Jacco H Snoeijer. Coalescence of bubbles in a viscoelastic liquid. *Physical Review Fluids*, 8(8):083603, 2023.
- [183] Álvaro Moreno Soto, Tom Maddalena, Arjan Fraters, Devaraj Van Der Meer, and Detlef Lohse. Coalescence of diffusively growing gas bubbles. *Journal of fluid mechanics*, 846:143–165, 2018.
- [184] Yuan-Hsuan Wu, Ho Bum Park, Teruhiko Kai, Benny D Freeman, and Douglass S Kalika. Water uptake, transport and structure characterization in poly (ethylene glycol) diacrylate hydrogels. *Journal of Membrane Science*, 347(1-2):197–208, 2010.
- [185] Hongyun Tai, Melissa L Mather, Daniel Howard, Wenxin Wang, Lisa J White, John A Crowe, Steve P Morgan, Amit Chandra, David J Williams, Steven M Howdle, et al. Control of pore size and structure of tissue engineering scaffolds produced by supercritical fluid processing. *Eur Cell Mater*, 14:64–77, 2007.
- [186] MT Hörantner, Wei Zhang, M Saliba, K Wojciechowski, and HJ Snaith. Templated microstructural growth of perovskite
-

- thin films via colloidal monolayer lithography. *Energy & environmental science*, 8(7):2041–2047, 2015.
- [187] Chengbiao Ge, Wentao Zhai, and Chul B Park. Preparation of thermoplastic polyurethane (tpu) perforated membrane via co2 foaming and its particle separation performance. *Polymers*, 11(5):847, 2019.
- [188] Carlo Marrazzo, Ernesto Di Maio, Salvatore Iannace, and Luigi Nicolais. Process-structure relationships in PCL foaming. *Journal of cellular plastics*, 44(1):37–52, 2008.
- [189] Elena Aionicesei, Mojca Škerget, and Željko Knez. Measurement of co2 solubility and diffusivity in poly (l-lactide) and poly (d, l-lactide-co-glycolide) by magnetic suspension balance. *The Journal of Supercritical Fluids*, 47(2):296–301, 2008.
- [190] Sara Coppola, Lisa Miccio, Zhe Wang, Giuseppe Nasti, Vincenzo Ferraro, Pier Luca Maffettone, Veronica Vespini, Rachele Castaldo, Gennaro Gentile, and Pietro Ferraro. Instant in situ formation of a polymer film at the water–oil interface. *RSC advances*, 12(48):31215–31224, 2022.
- [191] Fiona C Meldrum and Cedrick O’Shaughnessy. Crystallization in confinement. *Advanced Materials*, 32(31):2001068, 2020.
- [192] Atefeh Khaleghi, Seyed Mojtaba Sadrameli, and Mehrdad Manteghian. Thermodynamic and kinetics investigation of homogeneous and heterogeneous nucleation. *Reviews in Inorganic Chemistry*, 40(4):167–192, 2020.
- [193] Chang Dae Han and Chin-Yuan Ma. Foam extrusion characteristics of thermoplastic resin with fluorocarbon blowing agent. i. low-density polyethylene foam extrusion. *Journal of applied polymer science*, 28(9):2961–2982, 1983.
- [194] Chin-Yuan Ma and Chang Dae Han. Foam extrusion characteristics of thermoplastic resin with fluorocarbon blowing agent.
-

- ii. polystyrene foam extrusion. *Journal of applied polymer science*, 28(9):2983–2998, 1983.
- [195] Ajay Kumar Jena, Ashish Kulkarni, and Tsutomu Miyasaka. Halide perovskite photovoltaics: background, status, and future prospects. *Chemical reviews*, 119(5):3036–3103, 2019.
- [196] Satyajit Gupta, David Cahen, and Gary Hodes. How *snf2* impacts the material properties of lead-free tin perovskites. *The Journal of Physical Chemistry C*, 122(25):13926–13936, 2018.
- [197] Feng Hao, Constantinos C Stoumpos, Peijun Guo, Nanjia Zhou, Tobin J Marks, Robert PH Chang, and Mercouri G Kanatzidis. Solvent-mediated crystallization of $\text{ch}_3\text{nh}_3\text{sn}_2\text{i}_3$ films for heterojunction depleted perovskite solar cells. *Journal of the American Chemical Society*, 137(35):11445–11452, 2015.
- [198] Yue Yu, Dewei Zhao, Corey R Grice, Weiwei Meng, Changlei Wang, Weiqiang Liao, Alexander J Cimaroli, Hongmei Zhang, Kai Zhu, and Yanfa Yan. Thermally evaporated methylammonium tin triiodide thin films for lead-free perovskite solar cell fabrication. *RSC advances*, 6(93):90248–90254, 2016.
- [199] Xiao Liu, Tianhao Wu, Jung-Yao Chen, Xiangyue Meng, Xin He, Takeshi Noda, Han Chen, Xudong Yang, Hiroshi Segawa, Yanbo Wang, et al. Templated growth of fasni_3 crystals for efficient tin perovskite solar cells. *Energy & Environmental Science*, 13(9):2896–2902, 2020.
- [200] Guixiang Li, Zhenhuang Su, Laura Canil, Declan Hughes, Mahmoud H Aldamasy, Janardan Dagar, Sergei Trofimov, Luyao Wang, Weiwei Zuo, José J Jerónimo-Rendon, et al. Highly efficient pin perovskite solar cells that endure temperature variations. *Science*, 379(6630):399–403, 2023.
- [201] Huiyin Zhang, Jiangjian Shi, Lifeng Zhu, Yanhong Luo, Dongmei Li, Huijue Wu, and Qingbo Meng. Polystyrene stabilized perovskite component, grain and microstructure for improved
-

- efficiency and stability of planar solar cells. *Nano Energy*, 43:383–392, 2018.
- [202] Mozhgan Yavari, Mohammad Mazloun-Ardakani, Somayeh Gholipour, Mohammad Mahdi Tavakoli, Nima Taghavinia, Anders Hagfeldt, and Wolfgang Tress. Reducing surface recombination by a poly (4-vinylpyridine) interlayer in perovskite solar cells with high open-circuit voltage and efficiency. *ACS omega*, 3(5):5038–5043, 2018.
- [203] Antonella Giuri, Sofia Masi, Andrea Listorti, Giuseppe Gigli, Silvia Colella, Carola Esposito Corcione, and Aurora Rizzo. Polymeric rheology modifier allows single-step coating of perovskite ink for highly efficient and stable solar cells. *Nano Energy*, 54:400–408, 2018.
- [204] Yicheng Zhao, Jing Wei, Heng Li, Yin Yan, Wenke Zhou, Dapeng Yu, and Qing Zhao. A polymer scaffold for self-healing perovskite solar cells. *Nature communications*, 7(1):10228, 2016.
- [205] Jianfang Qin, Yangjie Chen, Xiaowei Guo, Haiying Yang, Yinglian Qin, Chenzhong Yao, Baohua Lv, Yiyan Bai, and Yan Zhan. A polymer strategy toward high-performance multifunctional perovskite optoelectronics: From polymer matrix to device applications. *Advanced Optical Materials*, 11(7):2202809, 2023.
- [206] Justin G Kennemur. Poly (vinylpyridine) segments in block copolymers: Synthesis, self-assembly, and versatility. *Macromolecules*, 52(4):1354–1370, 2019.
- [207] Piotr Matczak. $N \rightarrow sn$ coordination in the complexes of tin halides with pyridine: A comparison between sn (ii) and sn (iv). *Applied Organometallic Chemistry*, 33(4):e4811, 2019.
- [208] Francesco Lamberti, Teresa Gatti, Enrico Cescon, Roberto Sorrentino, Antonio Rizzo, Enzo Menna, Gaudenzio Meneghesso,
-

- Moreno Meneghetti, Annamaria Petrozza, and Lorenzo Franco. Evidence of spiro-ometad de-doping by tert-butylpyridine additive in hole-transporting layers for perovskite solar cells. *Chem*, 5(7):1806–1817, 2019.
- [209] Giuseppe Nasti, Mahmoud Hussein Aldamasy, Marion Alwine Flatken, Pellegrino Musto, Piotr Matczak, André Dallmann, Armin Hoell, Artem Musiienko, Hannes Hempel, Ece Aktas, et al. Pyridine controlled tin perovskite crystallization. *ACS Energy Letters*, 7(10):3197–3203, 2022.
- [210] Shizuo Arichi. Studies of poly-2-vinylpyridine. iii. intrinsic viscosity and molecular weight. *Bulletin of the Chemical Society of Japan*, 39(3):439–446, 1966.
- [211] Priyanka Roy, Numeshwar Kumar Sinha, Sanjay Tiwari, and Ayush Khare. Influence of defect density and layer thickness of absorption layer on the performance of tin based perovskite solar cell. In *IOP conference series: materials science and engineering*, volume 798, page 012020. IOP Publishing, 2020.
- [212] Wen Liang Tan and Christopher R McNeill. X-ray diffraction of photovoltaic perovskites: Principles and applications. *Applied Physics Reviews*, 9(2), 2022.
- [213] Yingxia Zong, Yuanyuan Zhou, Yi Zhang, Zhipeng Li, Lin Zhang, Ming-Gang Ju, Min Chen, Shuping Pang, Xiao Cheng Zeng, and Nitin P Padture. Continuous grain-boundary functionalization for high-efficiency perovskite solar cells with exceptional stability. *Chem*, 4(6):1404–1415, 2018.
- [214] Yang Bai, Yun Lin, Long Ren, Xiaolei Shi, Ekaterina Strounina, Yehao Deng, Qi Wang, Yanjun Fang, Xiaopeng Zheng, Yuze Lin, et al. Oligomeric silica-wrapped perovskites enable synchronous defect passivation and grain stabilization for efficient and stable perovskite photovoltaics. *ACS Energy Letters*, 4(6):1231–1240, 2019.
-

-
- [215] Bhumika Chaudhary, Ashish Kulkarni, Ajay Kumar Jena, Masashi Ikegami, Yosuke Udagawa, Hideyuki Kunugita, Kazuhiro Ema, and Tsutomu Miyasaka. Poly (4-vinylpyridine)-based interfacial passivation to enhance voltage and moisture stability of lead halide perovskite solar cells. *ChemSusChem*, 10(11):2473–2479, 2017.
- [216] Heon Jin, Michael D Farrar, James M Ball, Akash Dasgupta, Pietro Caprioglio, Sudarshan Narayanan, Robert DJ Oliver, Florine M Rombach, Benjamin WJ Putland, Michael B Johnston, et al. Alumina nanoparticle interfacial buffer layer for low-bandgap lead-tin perovskite solar cells. *Advanced Functional Materials*, 33(35):2303012, 2023.
- [217] Sara Covella, Vincenza Armenise, Muhammad Okash Ur Rehman, Ece Aktas, Francesco Fracassi, Fabio Palumbo, Silvia Colella, Antonio Abate, and Andrea Listorti. Plasma-based modification of tin halide perovskite interfaces for photovoltaic applications. *ACS Applied Materials & Interfaces*, 2024.
- [218] Yali Chen, Yu Tong, Feng Yang, Tianxiang Li, Wan Li, Heng Qi, Ziyong Kang, Hongqiang Wang, and Kun Wang. Modulating nucleation and crystal growth of tin perovskite films for efficient solar cells. *Nano Letters*, 24(18):5460–5466, 2024.
-

