

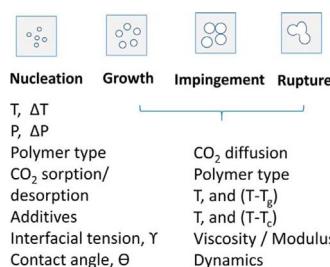
Foaming of polymers with supercritical fluids and perspectives on the current knowledge gaps and challenges

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GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, we examine the state of the art of the physical foaming of polymers with supercritical fluids with a primary focus on carbon dioxide. We provide a critical analysis of the current research pathways and the main scientific open questions. We discuss the knowledge gaps along with technological challenges for further advances. Perspectives on the foaming of amorphous and semi-crystalline polymers, polymer blends, copolymers, and thermosetting polymers are presented. Challenges pertaining to the improved understanding of the nucleation phenomena and the limitations on the modeling and processing methodologies are discussed.

1. Introduction

Foams are multiphase materials in which one phase is in the gaseous state. They are versatile materials encountered in nature from bones to tree trunks, as well as everywhere in our daily life, from our cars to beds. The reason for their ubiquity is the set of properties that arise from their *cellular* structure which gives them a wide range of functional attributes. They are effective materials for thermal insulation, sound absorption, separation media, controlled release drug formulations, tissue engineering scaffolds, as well as structural materials that may be used in sporting goods or protective media as helmets, to mention a few. In thermal insulation applications, multitude of *closed-cells* acts as microscopic double-glazing units. The closed-cell

morphology impedes heat from flowing from one cell to another. This contrasts with acoustic absorption applications where the cells are interconnected. The *open-cell morphology* allows the sound waves to enter the structure and dissipate through multiple scattering within the foam. Pores need to be connected also in tissue engineering applications to allow for flow of nutrients and waste. In addition to the pore morphology, foam density also provides versatility. In thermal insulation applications pore sizes must be small to reduce the thermal conductivity. In tissue engineering scaffolds pores must be not only interconnected but also of sufficient size for effective cell attachment and proliferation.

Among the existing foams, polymeric foams represent the major part of the overall market, being worth more than US \$100 billion in

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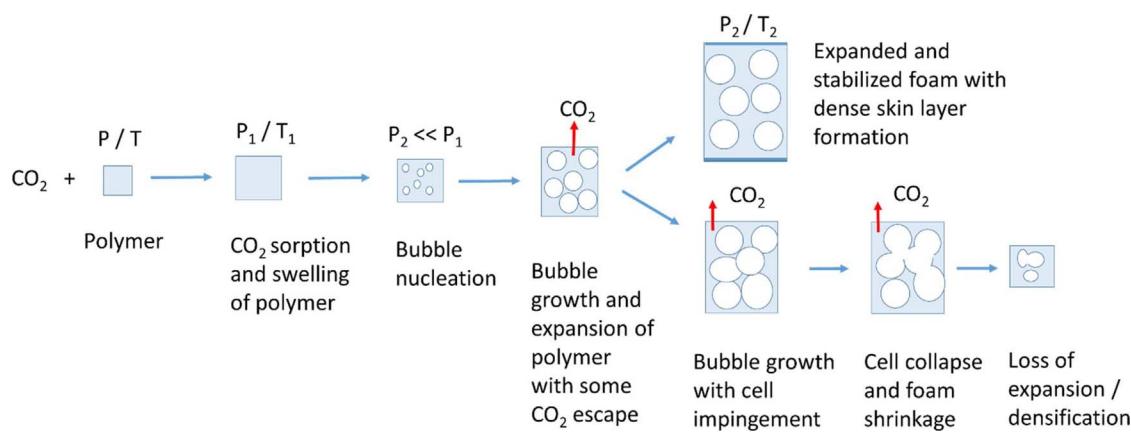


Fig. 1. Schematic illustration of the foaming process with CO_2 demonstrating CO_2 sorption, followed by the cell growth and expansion (leading to initial formation of isolated pores), cell impingement and cell-collapse (which, if can be controlled, may lead to interconnected pores, but if proceeds further, may lead to extensive cell collapse and densification). The outcomes depend on the sorption stage (pressure and temperature), decompression stage (rate of decompression), CO_2 diffusion coefficient under the prevailing P/T conditions, thermophysical state of the polymer system (the distance from and/or approach to the glass transition or melting temperature, i.e., whether glassy, rubbery or crystalline), and the dynamics of the changes in the rheological properties (viscosity, modulus) of the polymer.

2015 [1]. Polyurethanes and foams of other petroleum-based polymers like polystyrene, polypropylene and polyethylene dominate the overall market while foams based on biopolymers, like poly(lactic acid) and others derived from naturally occurring polymers such as cellulose and starch are increasing their market penetration [2].

The dominant and industrially relevant foaming technologies are (a) the *extrusion foaming* (with chemical as well as physical blowing agents), (b) the *bead foaming* (utilized principally with polystyrene, but more recently with polypropylene and poly(lactic acid)), and (c) the *injection molding foaming*. They all rely on the capability of the polymer to form polymer/gas solutions under pressure, and then undergo demixing that occurs upon pressure reduction or a rise in temperature that initiates bubble nucleation and growth.

Among the various physical foaming agents utilized, supercritical fluids, and in particular carbon dioxide, belong to a special class due to their pressure-tunable properties. Tunability of the properties presents opportunities in modulating the polymer-fluid interactions. Further attractiveness of using CO_2 is linked to the lowered burden on the environment compared to traditional blowing agents such as HCFCs, or greater safety offered compared to flammable hydrocarbons such as pentane.

Foaming with supercritical fluids, though conceptually simple, is a complex dynamic process requiring full appreciation of the fundamentals of polymer science, thermodynamics, physics and chemistry of solutions and interfaces, and interacting species as well as polymer materials and process engineering. In this manuscript, we draw a *fil rouge*, connecting the current state of knowledge on foaming with supercritical fluids (with carbon dioxide as the primary fluid of interest) with the actual development challenges, highlighting the knowledge gaps that must be filled to meet the challenges.

2. Current state

Foaming with supercritical fluids is a vibrant area of research and development. Several comprehensive review articles have already been published which cover the breadth of the field [3–9]. Among the recent trends are the formation of nanocellular foams [6,8,9], foaming of polymer blends [10,11], foaming of semicrystalline polymer and copolymers [12,13], elastomeric materials [14–16], high performance engineering plastics and composites [17,18] and sustainable foams and biofoams [2,19,20]. Here we provide the basic principles of foaming, briefly describe the typical processing technologies and the polymer properties relevant to foaming.

2.1. Basic principles of foaming

Carbon dioxide is the primary supercritical fluid that is employed as a physical blowing agent in generating polymer foams. However, other gases such as nitrogen, sometimes in conjunction with carbon dioxide are also utilized. The foaming process involves two basic steps which are (a) sorption or dissolution of carbon dioxide in the polymer matrix under pressure to form a polymer/gas *solution* and (b) bubble nucleation and growth upon a reduction in pressure (which is the common path) or an increase in temperature (if the sorption is done at relatively low temperatures). The bubble growth, and along with it, the foaming process ends before the mass transport comes to a complete end upon vitrification or crystallization of the polymer. Vitrification or crystallization prevents cell coalescence and stabilizes the cellular structure [8,21,22]. Depending upon the growth dynamics and the nature of the polymer, in the case of delayed vitrification, large extensional deformation of the cell-wall may result in the impingement of neighboring cells followed by cell-wall rupture and cell coalescence. Multiple coalescence phenomena may eventually cause the collapse of the whole foamed structure [23,24]. Both the morphology coarsening as a consequence of the cell coalescence and the densification as a consequence of the foam collapse are generally detrimental to the foam properties, and represent the major cause of foaming failure. Failure prevention strategies embrace the material recipe (polymer architecture, additives, blending, blowing agent nature and concentration, to mention a few) and the development of processing pathways. **Fig. 1** illustrates these concepts for a process in which the CO_2 sorption stage is followed by decompression. The main process parameters are the gas concentration, the temperature at which the thermodynamic instability promoting the bubble nucleation is induced and the mode in which the pressure reduction is carried out.

The outcomes, in terms of pore sizes and morphology, are intimately connected to (a) the concentration (upper bounded by gas solubility), (b) the diffusivity of CO_2 in the polymer matrix, (c) the interfacial tension of the polymer/ CO_2 solutions in contact with CO_2 , and (d) how the polymer transition temperatures (T_g and T_m or T_c), and the associated plasticization/vitrification and melting/crystallization processes and consequently how the rheological properties (viscosity, modulus) are affected both during the sorption and later during the decompression stage [5,25,26]. Other factors being equal, at a given temperature, faster decompression leads to smaller pore sizes or higher cell number densities. Similarly, from a given gas concentration and pressure drop rate, foaming from higher temperatures tend to lead to formation of larger pores, while the foam density first decreases and then increases with the temperature [27].

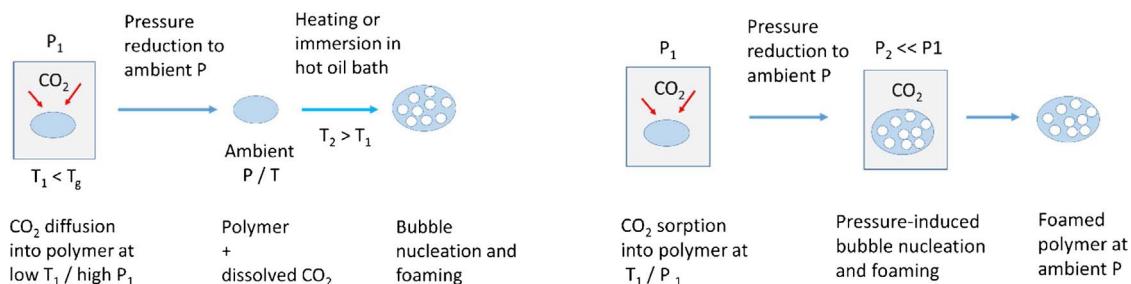


Fig. 2. Batch foaming. Solid state-foaming with sorption of CO_2 at low T ($T_1 \ll T_g$) but high P (P_1) followed by pressure reduction to ambient P , and heating ($T_2 \gg T_1$) (left); and pressure-induced foaming with sorption of CO_2 at high P and T (P_1 , T_1) followed by decompression ($P_2 \ll P_1$) (right).

2.2. Process options for foaming with supercritical fluids

Three most common foaming operations are the batch, the extrusion and the injection molding operations.

Batch foaming involves exposing a polymer sample to carbon dioxide in a high-pressure vessel (for a suitable time, depending upon the polymer/ CO_2 mutual diffusivity, to allow sorption) which is then followed by decompression upon which the gas bubbles are nucleated. If sorption is conducted at a relatively low temperature, after decompression the polymer may be too rigid to foam. The polymer can however be removed from the vessels as a solid matrix with CO_2 trapped in a metastable phase. The polymer can then be heated to soften the polymer to induce bubble nucleation and foaming. The foaming process conducted in this manner is a two-step process and is referred to as "solid-state foaming". These processes are illustrated in Fig. 2.

The batch process is extensively utilized in research (typically employing small sample sizes, in the order of a few grams, in the form of a disk) since it is relatively simple to carry out and allows a fine control of processing variables such as pressure, temperature and time. However, the process suffers from low productivity and as such has very limited use in industry where high production rates are often required. High-productivity is offered in **extrusion foaming**. As illustrated in Fig. 3, carbon dioxide is introduced into the extrusion barrel and mixed with the molten polymer, again at high pressure. In this case, however, the pressure is due to the pressure built up along with the polymer flow and not to the external gas pressure, as was the case in the batch process. At the nozzle exit, the polymer/ CO_2 solution experiences a rapid pressure drop undergoing CO_2 de-mixing and the associated bubble nucleation. Extrusion foaming is the industrially preferred option for foaming for its adaptability for continuous production and easier scaling-up potential. However, extrusion foaming introduces its own challenges which are linked to (a) the pressure limitations imposed by the extruder barrel at the CO_2 charge point, (b) time available for CO_2 sorption and dissolution in the polymer before the polymer exits from the nozzle, and (c) the melt viscosity requirements to prevent CO_2 escape and foam collapse after exiting the nozzle.

In extrusion foaming, CO_2 is used as a plasticizing agent that lowers the operational temperature and modifies the rheological properties of the melt which functions as the expansion agent as the polymer leaves the extruder [3,10,28]. The process is typically carried out with single or double screw systems, or in systems involving two extruders that are coupled in tandem. As the polymer travels through the die and exits, along with the pressure drop, there is an inevitable CO_2 loss which limits the degree of expansion (foaming). This becomes a major issue for polymers with low melt viscosity. A common approach is to freeze the outer layers (skin) which is implemented by lowering the temperature in the die. This presents a challenge in generating foams with high cell number densities since the rheological state of the polymer must permit bubble growth, yet should prevent cell coalescence. For example, polyolefins (such as high-density polyethylene, low density polyethylene and isotactic polypropylene) are known to be difficult to foam due to their low melt strength which is needed to sustain cell growth [10]. A plausible approach that is often considered is to increase the CO_2 sorption level in the extruder, as this would allow greater lowering of the viscosity to carry out the extrusion process at lower temperatures, so that when the melt leaves the die, it will have sufficient melt strength. *But, introducing high level of CO_2 presents a challenge with traditional extruders that are rectified for CO_2 -foaming. There is a need for a new generation of extruders that are specifically designed for foaming with carbon dioxide.*

Foam injection molding is regarded as a cost-effective and practical method for fabricating foams with complex, three-dimensional geometries. The technology is rapidly evolving to allow the required control of the expanding polymer/ CO_2 solution during the fast process cycles that are involved in injection molding [29,30]. In particular, avoiding premature foaming during injection (in the sprues and runners preceding the mold) is the major issue. For instance, to limit premature foaming and restrict foaming in the mold, foaming injection molding with core-back mold opening has been introduced. In this process, the mold cavity is first completely filled out with the polymer, and then a portion of the mold is suddenly moved along the thickness direction after a period of dwelling time. By expanding the cavity, the dissolved

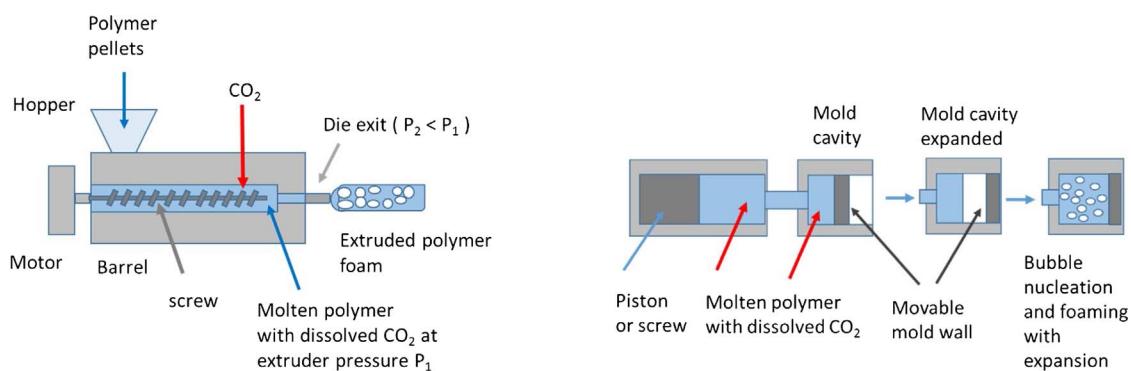


Fig. 3. Extrusion foaming (Left) and foam-injection molding (Right) processes. In extrusion foaming, expansion starts immediately after die exit. In injection molding, expansion is induced with enlarging the mold cavity after it is first filled with polymer + CO_2 solution.

gas in the polymer experiences a significant pressure drop and the foaming process starts uniformly in the entire injection-molded product. This is also illustrated in Fig. 3. A variation is the gas-laden pellet injection molding process [31] in which gas-laden polymer beads are first produced by extrusion foaming and pelletizing. These pellets (polymer beads) with entrapped CO₂ are then used as the feed polymer in the injection molding systems to generate the 3D-foamed objects.

2.3. Polymer types and polymer properties that play key roles

Foaming with CO₂ has been commonly carried out with glassy, amorphous polymers. Polystyrene, in particular, is the most frequently foamed polymer. Foaming of semi-crystalline polymers is more challenging, mainly due to the very narrow foam-processing window available, upper bounded by insufficient melt strength at high temperatures and lower-bounded by the incumbent crystallization at low temperatures. Furthermore, the sets of properties that a polymer has to have in order to be subjected to a gas-foaming process are: reasonable solubility of the blowing agent, high enough melt strength, and the availability of setting mechanisms (crystallization or vitrification) in the vicinity of the processing window. In this context, a valuable processing aid is the *plasticization* of the polymer brought about by the dissolved blowing agent. In the case of carbon dioxide this effect is especially significant [4,6,26,32–36]. For example, glass transition temperature of polystyrene is reduced from its neat, ambient T_g by about 50 °C when exposed to CO₂ at about 50 bar. Melting temperature of poly(ϵ -caprolactone) is reduced by about 25 °C when exposed to CO₂ at 100 bar. When the polymer/carbon dioxide solution exits the extruder nozzle, then, it experiences carbon dioxide desorption and, correspondingly, the loss of the plasticization effect, equivalent to a temperature quench, which tremendously helps foam setting and stabilization. Fig. 4 represents how the effective processing window (the T -range between T_g and T_c (or $T_{melting}$)) for foaming is expanded with plasticization in carbon dioxide in a semi-crystalline polymer. It further illustrates the importance of the processing temperature in view of the actual T_g and T_c in the presence of CO₂, in that the temperature difference ($T-T_g$) and ($T-T_c$) determine how quickly the polymer will vitrify, or crystallize which will affect the cell growth dynamics or the approach to stabilized foams. In amorphous polymers not displaying T_c (or $T_{melting}$), T_g is simply lowered. Along with lowering of T_c , the melt processing temperature is lowered, thereby expanding the melt process window by $T_{cP}-T_{c0}$, which is important in extrusion foaming.

Along with these changes that accompany sorption and later desorption of carbon dioxide, viscosity of the polymer matrix is also changed (lowered with sorption, increased with desorption). Viscoelastic properties of the polymer matrix in the presence of dissolved carbon dioxide play an extremely significant role in the final outcomes. During cell nucleation and growth, the viscosity of the

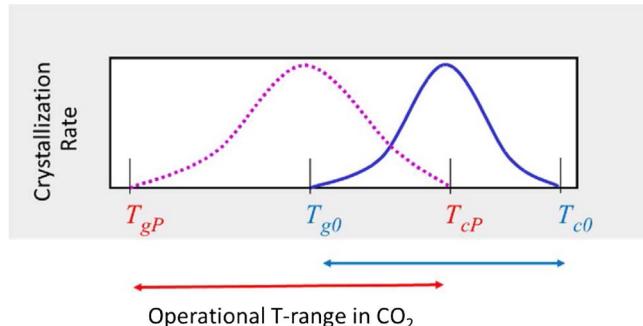


Fig. 4. The decrease in the ambient pressure crystallization (or melting) temperature (T_{c0}) and the glass transition temperature (T_{g0}) of the polymer in the presence of dissolved carbon dioxide at pressure P to T_{cP} and T_{gP} . The operational temperature range is expanded in the presence of carbon dioxide. The effective processing windows for both solid and melt extrusion foaming are expanded.

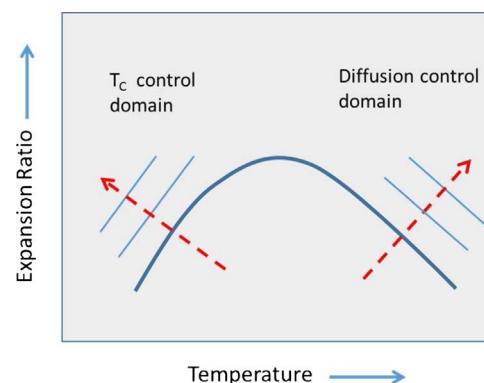


Fig. 5. Influence of crystallization temperer and the diffusivity of carbon dioxide as competing factors affecting the expansion ratios that can be achieved. [Adopted from ref. 37].

medium must be low enough to permit expansion, but high enough to prevent escape of CO₂ from the outer boundaries which would otherwise lead to cell collapse. In foaming of semi-crystalline polymers, the foaming pressure and temperature plays an important role also as they affect not only the domains (above T_g or above T_m) in which the foaming proceeds, but equally influence the role the crystalline domains and the rate of crystallization would play in stabilizing the foams generated.

Fig. 5 is a schematic representation of the competing factors that come into play when foaming semicrystalline polymers. Crystallization temperature (T_c), thus solidification is altered in CO₂ depending upon the sorption level which depends on P/T . If T_c is significantly lowered, and if ($T_{foaming} - T_c$) difference is large, solidification is slowed down which allows for CO₂ loss through extended diffusion from the foam and leads to densification. If T is not high enough, and the modulus of the polymer matrix or the viscosity are high, then CO₂ diffusion is slow which results in limited cell growth leading to closed cell structures. Solidification occurs too quickly before foam is fully expanded. If the foaming temperature is high, then there is high CO₂ diffusivity which leads to large pores, high expansion ratios. But, if the foaming temperature is too high, then significant gas loss to surroundings lead to cell collapse and foam shrinkage and densification unless solidification is rapid. The challenge is the identification of optimal processing conditions that will lead to desired expansion ratios which, as illustrated in Fig. 5 goes through a maximum with temperature of foaming [37].

3. Knowledge gaps and current challenges

Numerous applications of the polymeric foams point to various development needs. This section highlights the main knowledge gaps that need to be filled to address the current challenges in foaming towards increasing performance, decreasing cost and improving sustainability.

3.1. Determination of the amount of CO₂ dissolved in the polymer

At present, there is no robust experimental technique to readily determine the amount of CO₂ that dissolves in a given polymer at a given pressure and temperature. The complications arise from the swelling that accompanies CO₂ sorption. The change in mass of the polymer exposed to CO₂ can be determined but if it cannot be accurately corrected for buoyancy, the results are suspect. Density of CO₂ at different temperatures and pressures are well known (for example through the NIST data base), but the volume of the polymer at the corresponding P , T conditions is not easy to assess experimentally. A technique based on in situ thickness measurement using a spectroscopic reflectometer has been reported to provide swelling ratios for thin films (150–300 nm) that are solution cast on silicon wafers, provided corrections can be incorporated for window effects [38]. A significant

amount of publications has relied on modeling such as the Sanchez-Lacombe model to estimate the swelling of polymers to use in the buoyancy corrections [39,40]. But, modeling has its limitations and their reliability need to be verified independently by experimentation.

A versatile instrument that is commonly employed to assess CO₂ sorption is the Rubotherm magnetic suspension balance. The instrument has been modified by several laboratories to visually observe the polymer sample during exposure to CO₂ to determine the degree of swelling [41–43]. The approach is to put a sample of known initial shape, i.e., a cylindrical rod or disk along with a scale bar and then record the change in, for example the height of the sample, using a cathetometer, or its overall shape and radius using a camera. Even though this sounds simple, there are complications, as the change in the polymer shape and boundaries are not necessarily uniform in all directions. Another approach that has been recently developed is to attach a spherical bead to a rod and measure the change in the radius to assess the swelling. The technique however becomes limited to use over wide range of pressures or temperatures as the polymer may soften and the integrity of the shape may be lost. Another limitation arises from the possible extraction of the low molecular weight fractions by the dense CO₂ phase, which reduces the sample weight during the test, thus leading to erroneous measurements [44,45]. *Accurate determination of CO₂ sorption is an outstanding problem needing a solution that can be broadly used with any type of polymer.*

3.2. Depression of T_g and T_m and its connection to the CO₂ sorption level

For a range of amorphous and semi-crystalline polymers T_g and T_m values are available in the literature as a function of temperature and pressure. In this regard, among the polymers for which data is frequently reported are poly(methyl methacrylate), polystyrene and polyesters such as poly(ϵ -caprolactone), poly(lactic acid) [32–36,46]. Measurements are based on determinations using either a high-pressure differential scanning calorimeter (DSC) unit, or the assessments of the changes in the transmitted light intensity or the mechanical properties, or monitoring the frequency shift using quartz crystal resonators (QCR). The measurements based on light transmission while effective in determining the melting or crystallization transitions with high degree of detail, are not as suitable for the assessment of the glass transition temperatures. An important shortcoming of all these measurements is the missing link between the transition temperature and the amount of CO₂ absorbed in the polymer at those conditions.

Knowledge of the level of CO₂ in the polymer matrix at a given P,T condition is extremely important. It would provide a better understanding of the dynamics of the polymer behavior such as the rate of approach to the transition temperatures and the changes in the viscosity or other viscoelastic properties of the polymer during the decompression process.

3.3. Viscoelastic properties and melt viscosity

Even though determination of T_g and T_m of polymers under CO₂ pressure has been explored for several polymers, data on the viscoelastic properties other than melt viscosity is scarce. Only limited experimental data is available on the change of, for example, the modulus with CO₂ pressure at a given temperature [26,47]. Such information would be of high value in advancing our understanding the dynamics of cell nucleation and bubble growth. There are distinct consequences of foaming conditions and the polymer viscoelastic properties on the surface morphology of the foams. The bubble growth near the surface layers may lead to surface protrusions (blisters) which tend to rupture if the melt viscosity is not sufficiently high [48]. If the viscosity is low, rapid diffusion of CO₂ from near the surface regions leads to rise in T_g and modulus leading to dense skin layers. The thickness of these layers is influenced by the rate at which the changes in transition temperatures are approached and the moduli are altered in CO₂ during decompression.

It is a challenge to experimentally determine the modulus and rigidity, thermal transitions (both T_g and T_m) and their variation with CO₂ pressure and temperature for a polymer system all in the same instrument without changing the polymer loading and configuration.

3.4. Pore morphology

The way pores are located within the polymeric matrix, their size distribution, shape, number density, interconnectivity, the shape of the strut among the pores, the shape of the wall between two pores, are all attributes of the pore morphology which influence the final foam properties. One of the achievements of the 80's and 90's was the observation that most foam properties improve with the pore size reduction. Microcellular foams were then introduced, characterized by cell sizes of the order of tens or hundreds of microns. Nowadays, nanocellular foams have been achieved with few polymers and represent a major research goal for commodity plastics. Another morphological feature that is of great interest is the degree of interconnectivity. Cell-wall opening mechanisms are today under consideration, focusing on the interplay among ultimate rheological properties (melt strength), presence of solid (cell wall breaker) and fluid (inducing phase separations) additives and the processing conditions as the key factors [49].

If the bulk viscosity or the rigidity of the polymer is not sufficiently low, the cells that are nucleated may not grow much and the final morphology of the foam is then usually that of isolated pores. If the cell number density is sufficient, and the viscosity of the medium permits cells to grow and impinge upon each other, there is the potential of forming an interconnected pore morphology. If however, cells grow further they can coalesce and lead to large voids, leading to a non-uniform pore distribution and may display a bimodal morphology. If there is compositional gradient in the polymer matrix which may for example naturally arise in blends, or a temperature gradient which may develop during decompression as a result of Joule-Thompson like cooling occurring at the outer surface, a gradient pore morphology may develop [50]. In copolymers and blends, differences in the behavior of the domains that interact more with carbon dioxide may lead to pore size and morphology differences in the foam generated. Depending upon the application area, the requirements for pore morphology and size are distinctly different. For example, as noted earlier, while isolated pores are desirable for insulation, interconnected pores are required for sound insulation or for foams that can be used as biomedical scaffolds for tissue engineering.

It is currently a challenge to a priori select the pressure/temperature conditions to achieve a target pore size, pore size distribution, pore morphology, cell number density, and overall foam bulk density for a given polymer matrix.

3.5. Foaming of polymers with low glass transition temperatures

Foaming of rubbers with T_g below room temperature presents challenges in producing stable foams with reasonable mechanical strength. These materials are soft with low rigidity, and as such their viscoelasticity must be balanced to prevent coalescence of growing bubbles. They may display post-expansion at room temperature if residual CO₂ remains in the matrix, or may undergo post-foaming shrinkage due to the escape of CO₂ from the matrix which is above its T_g [48,51]. This is an area requiring further research to develop new strategies.

Current methodology is either crosslinking or blending the polymer with another polymer which may act as hard domains, bringing rigidity and dimensional stability to the polymer matrix and the resulting foam [52,53]. The studies involving rubbers have been limited, with recent activities having been reported primarily with silicone rubber [53], and copolymers of polyethylene such as poly(ethylene-co-propylene) [52,54,55]. A more comprehensive work has been recently conducted on poly(ethylene-co-vinyl acetate), poly(ethylene-co-vinyl acetate-co-

carbon monoxide) and their blends [48].

These polymers being elastomeric in nature have T_g values that are much lower than ambient temperature. In the presence of carbon dioxide their T_g is presumably lowered even further. These polymers are however semi-crystalline. The crystalline domains act as anchors for the amorphous chain domains which are in their rubbery state above T_g . In foaming of elastomers with T_m that are above room temperature but not too high, upon decompression significant initial volume expansions are expected, however as was noted with poly(ethylene-co-vinyl acetate) foams, this often follows by relaxation and shrinkage until reasonable degree of re-crystallization can be reached [48].

A current challenge with rubbery polymers and elastomers is to achieve the high expansions, yet at the same time be able to hinder the post-relaxation and shrinkage to generate stable foams with very low foam bulk densities.

3.6. Foaming of thin films

Foamed multilayer structures are of interest in various applications ranging from ultralow-k dielectrics to membranes for audio systems, or media for sound absorption [56,57]. However, foaming of thin films present experimental challenges. Even though CO_2 sorption times are shortened, during decompression, the CO_2 can easily escape and not lead to foaming of the polymer. Foaming then requires implementing measures that will hinder rapid CO_2 escape, which is sometime achievable under confining geometry [58]. However, current activity in foaming under confinement is not extensive. A different approach to foaming of thin films that has been reported is limited to template foaming using fluorinated block copolymers such as polystyrene-b-poly(perfluoroctylethyl methacrylate) in which the fluorinated blocks localize and stabilize the CO_2 bubbles [59].

3.7. Foaming of blends

Polymer blends are important for creating new materials with synergistic effects. Numerous high-performance applications in the automotive, transport and aerospace applications extensively employ blends where reducing the weight is an important factor. In foaming of blends with carbon dioxide several important factors come into play which arise from the nature of the polymers and whether or not they form miscible or immiscible blends, and how the miscibility is altered with temperature. Thermodynamically, entropy of mixing in polymer blends is small, and miscibility largely depends on the enthalpy of mixing which becomes favorable in systems in which attractive (exothermic) interactions such as hydrogen bonding take place. Other factors such as the shear rate, the viscosity ratio, blending ratio, interfacial tension affect the degree of dispersion [60]. The more common scenario is that of an immiscible blend which, depending upon the composition, will display an island (dispersed phase) and sea (continuous phase) morphology descriptive of the minor and major components of the blend, or a co-continuous morphology. Miscible blends show a single glass transition temperature intermediate to those of the blend constituents. Phase separation in blends typically develops when temperature is changed and phase boundaries are crossed. When exposed to carbon dioxide, due considerations must then be given not only to how CO_2 is sorbed in different domains, but how the miscibility boundaries are altered with pressure, temperature and the CO_2 sorption levels.

Another important factor is the thermal transitions of the component polymers and how they are altered in the presence of carbon dioxide. How bubble nucleation is initiated and proceeds in different domains, how they are affected by the presence of other domains create a complex picture that must be fully appreciated. For example, in blends of polystyrene with polypropylene, when CO_2 is introduced, a reduction in the size of the dispersed (minor) PS phase is reported [60]. In blends of PMMA with PS, dispersed PMMA rich phase is known to decreases with higher affinity to carbon dioxide [61]. Whenever

feasible, conditions that promote greater level of CO_2 dissolution in the component with higher viscosity facilitate the processing in extrusion foaming.

Often polymers are blended with a polymer that has higher affinity to carbon dioxide, with typical examples including but not limited to siloxane, or perfluorinated, or acrylic polymers. A related scenario is encountered when an amorphous polymer is blended with a semi-crystalline polymer [17], or when a glassy polymer is blended with an elastomer. Efforts also go into improving interfacial compatibility which improves gas retention for improved cell growth [60,62]. Presence of the incompatible interface domains in polymer blends may actually be a desirable feature as they help (heterogeneous) cell nucleation with a lower energy barrier [10]. The questions that were raised in the previous section for extrusion foaming with respect to rheological properties and melt strength are also important in foaming of blends. For example, blends of low density polyethylene and polypropylene suffer from cell collapse during cell-growth stage [10]. Another factor that needs to be considered is the diffusion of CO_2 in different domains. From a rheological point of view, the viscosity ratio of the constituent polymers play an important role as blending is promoted when the viscosities are close to each other, that is, the viscosity ratio approaches one.

The effect of blend compatibility, morphology and phase structure in foaming of blends with carbon dioxide has not yet been fully investigated.

3.8. Foaming of copolymers

Copolymers are different from blends in that polymeric constituents are not mixed by physical means, but are chemically linked. Random copolymers normally behave similar to their miscible physical mixed analogues. However, block copolymers are different. They chemically bring together otherwise incompatible polymer blends. The nature of phase separation is different. Here, the thermodynamically incompatible chains lead to micro-phase separated domains. This is a consequence of block copolymers undergoing self-organization. The outcome is the formation of domains that exhibit order, which may appear as spheres, cylinders, bi-continuous channels or alternating lamellae [63,64]. In contrast to the domain sizes in phase-separated blends (which may be in the order of 100 nm to 10 μm), the domain sizes in the micro-phase separated block copolymers are small, in the order of 10–100 nm. Whereas blends show upper or lower critical miscibility temperatures (UCST, or LCST), block copolymer display temperature dependent (upper or lower) order-disorder transitions (UODT or LODT). Carbon dioxide lowers not only the T_g of amorphous polymers, the T_m of semicrystalline polymers, but also influences the order-disorder transitions in block copolymers [65–67]. There is currently not much work focused on how these transitions are affected and the time scales associated with the dynamics of these transitions in the presence of carbon dioxide, and how they influence the final morphologies that are developed in foaming.

Some of the work, as in the case of blends, has aimed at incorporating CO_2 -philic polymer blocks such as fluorinated blocks as in the case of polystyrene-b-poly(perfluoroctylethyl methacrylate) in the copolymer [68]. Nanocellular foamed films could be generated by carrying out the depressurization at temperatures below the T_g of polystyrene, thereby restricting the foaming to the fluorine containing micro domains [65] which is schematically illustrated in Fig. 6. Similarly, in the block copolymer polystyrene-b-poly(methyl methacrylate), PMMA domains act as the domains with greater affinity to carbon dioxide [69]. The T_g of the PMMA domains is lowered more than the T_g of the polystyrene domains. The final morphology depends on the conditions of foaming. If the decompression conditions are such that PMMA is rubbery and PS is glassy, the bubble growth is restricted by the glassy PS matrix. The swelling of the CO_2 -philic domain and consequently the overall expansion ratio is also restricted unless the glassy domain undergoes deformation under the high swelling pressure of the CO_2 -philic

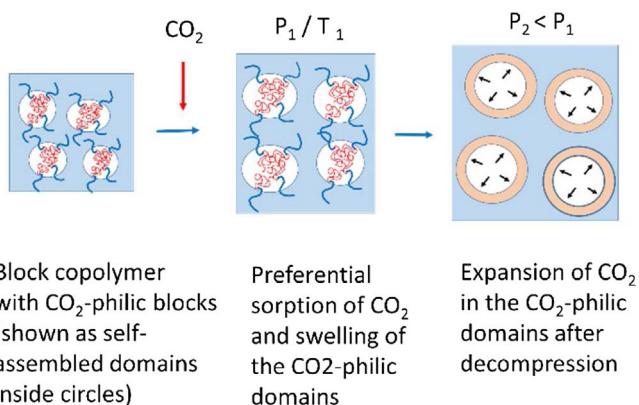


Fig. 6. Foaming of a di-block copolymer with a CO_2 -philic block. Carbon dioxide sorption and later the bubble nucleation primarily occurs in the CO_2 -philic domains.

domain. If the conditions are such that the non- or the less CO_2 -philic domain (such as the PS domain in this case) is initially also in the rubbery state and does not rapidly vitrify and remains in its rubbery state during the decompression stage, the nano-sized cells are expected to grow rapidly and potentially coalesce, forming larger pores. As CO_2 escapes from the matrix, the foamed system may undergo shrinkage with the collapse of cells. It should be noted that during the CO_2 sorption stage, the non- CO_2 -philic domains must be at temperatures that make those blocks reach their rubbery state for effective diffusion of CO_2 to the CO_2 -philic domains.

In di-block copolymer of polyethylene and polyethylene oxide, PEO domains serve as the CO_2 -philic block [64]. The polymer displays domain morphologies that may be spherical, lamellar or aligned lamellar. It has been shown that lamellar PE-b-PEO (with aligned poly(ethylene oxide) domains) leads to open cell structures, whereas PE-b-PEO with spherical PEO domains leads to closed cell structures at low temperatures, but mesh like opening at high temperatures.

A recent study on block copolymers report on the foaming of di-block copolymers with hydrophobic and hydrophilic blocks such as polystyrene-b-poly(4-vinyl pyridine) and poly(4-methyl styrene)-b-poly(4-vinyl pyridine) with mixtures of water and carbon dioxide as blowing agents [70]. Here polystyrene is the hydrophobic block. The results are reported to be the formation of open-celled di-block copolymers. *This study is of significance in that preparation of open-cell structured foams in general, and open cell foams using block copolymers in particular, is an area not well explored.* Use of two blowing agents is a common procedure when neither blowing agent can achieve the desired outcomes alone. Foaming of poly(lactic acid), or other biomedical polymers like poly(p-dioxanone), or poly(ϵ -caprolactone-co-lactide) in mixtures of carbon dioxide and acetone has been reported to promote the formation of connected, open-cell morphologies [71,72]. Another example is the foaming of polystyrene-b-poly(2-vinyl pyridine) with a mixture of carbon dioxide and methanol [73]. It has been shown that methanol with its strong affinity for PVP micro-domains, when introduced with CO_2 , can be localized in the PVP domain. With proper selection of the processing pressure and temperatures the T_g of polystyrene can be lowered to a level to permit initial bubble growth in the PVP domain, yet with a rapid rise of the T_g during depressurization, restrict the bubble growth and prevent the nanopores from collapsing.

Block copolymers with CO_2 -philic blocks can be foamed to generate nanoporous materials. They can also be blended with homopolymers and be transformed to nanoporous materials. The spherical micelles that form when the copolymer self-assembles serve as nucleation agents. Examples include foams of blends of poly(methyl methacrylate) with the triblock copolymer poly(methyl methacrylate)-b-poly(butyl acrylate)-b-poly(methyl methacrylate) [74,75] in which nucleation preferably takes place in the triblock copolymer nanostructures due to its high CO_2 -philicity, lowered surface tension, and the morphology.

These triblock copolymers develop a core-shell structure with the poly(butyl acrylate) block acting as the effective nucleation agent.

Copolymerization of ethylene with norbornene leads to cyclic copolymers with an opportunity to create polymers with low and high T_g which is achieved by altering the norbornene content in the copolymer [76,77]. The incorporation of norbornene prevents crystallization of polyethylene, and allows for improved foaming [76]. These studies show that under similar carbon dioxide concentrations, higher T_g cyclic olefin copolymer foams show higher cell nucleation densities with smaller cell sizes.

3.9. Foaming of thermosetting polymers

Thermosetting foams such as polyurethane, polyisocyanurate, phenol-formaldehyde, urea-formaldehyde, epoxy and silicone foams, are widespread and typically used for thermal insulation and packaging. For their production, the curing process occurs concurrently with a foaming process. In the past, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and flammable hydrocarbons (HCs) (e.g. pentane) have been used. To reduce the environmental impact and improve safety, CO_2 is now becoming important also in thermosetting foams. It has already been employed at lab scale to produce epoxy [78–80] and polyurethane foams [81,82]. Their development and exploitation has, however, an intrinsic difficulty which stems from the need for either the CO_2 sorption or the CO_2 release stages to chase the curing/polymerization reaction. Polymerization proceeds with its kinetics or characteristic time, τ_{polym} . Sorption has its own characteristic time which depends on the polymer/gas mutual diffusivity (τ_D) and the gas foaming process employed (τ_{foam}). Typically, $\tau_D \gg \tau_{\text{polym}} \gg \tau_{\text{foam}}$. As complete sorption has to precede polymerization (since no foaming is possible on a cured solid polymer), the requirement that $\tau_D \gg \tau_{\text{polym}}$ immediately poses a problem. In the case of epoxies, as the curing temperature is usually above room temperature, by reducing the temperature it is possible to slow down the polymerization reaction to give time for sorption. However, in other cases, like the polyurethanes, lowering the temperature is not feasible, and gas foaming is then limited only to samples with very small thickness to reduce the time for mass transport ($\tau_D \approx L^2/D$, where L is the characteristic length of the product to be foamed and D is the polymer/gas mutual diffusivity). These options are however not practical at industrial level. Another difficulty arises during the foaming stage. As $\tau_{\text{polym}} \gg \tau_{\text{foam}}$ (in practice, gas foaming is essentially instantaneous with respect to polymerization), the proper timing for gas release has to be chosen at a certain extent of the polymerization reaction. If gas release (and corresponding foaming) occurs early with respect to τ_{polym} , the polymer will have low viscosity and not be able to sustain the newly formed cellular structure, which will collapse after foaming stage. If, conversely, gas release occurs at the latest stage of polymerization, expansion ratios will be very limited. Several investigations have addressed these issues. For instance, investigation of the effect of the polymerization extent (in terms of the gel fraction) and the molecular weight between crosslinks, M_C , on CO_2 -foaming of epoxy resins highlight that the gel fraction description is not a sufficient parameter to assess the foaming capability of a resin, and that a minimum M_C is needed to allow the bubble to nucleate [79]. Finally, the sorbed blowing agent (in particular, CO_2) may have profound effects on the polymerization reaction, eventually modifying τ_{polym} [83]. *The current literature [78–84] shows that the educated use of CO_2 as a physical blowing agent in thermosetting polymers is well behind that of thermoplastics and has to be tackled in the future to allow for its effective utilization in foaming of thermosetting resins.*

3.10. Nucleating agents and homogeneous vs heterogeneous nucleation

In the industrial practice of thermoplastic foaming use of nucleating agents is of vital importance to control the final foam morphology. In fact, within the framework of classical nucleation theory, the presence

of a heterogeneity in the polymer/gas solution partially provides for the new nuclei interface, leading to a significant reduction of the free energy threshold that has to be overcome to form the nuclei.

Nucleation is the formation of the nucleus, the first new phase (bubble) within the parent metastable polymer + carbon dioxide matrix. The new phase thermodynamically has a free energy lower than the parent phase and the process is driven by the difference in the free energy between the two phases. The classical nucleation theory makes several assumptions among which are that nucleus (bubble) is a spherical droplet, and that instantaneous pressure drop leads to instantaneous nucleation and as such does not account for the effect of pressure drop rates, and further assumes that the bubble interface is an infinite flat planar surface. The limitations of the theory are recognized, but still provides insights into bubble nucleation and growth in systems that are undergoing both homogeneous and heterogeneous nucleation [9,25,85–87]. The stability of the nucleated bubble depends on the radius of the nucleus (R), the pressure difference (ΔP) between the internal bubble pressure and the pressure surrounding the sample, and the interfacial (surface) energy (γ). For homogeneous nucleation, the Gibb's free energy is then given by

$$\Delta G = -(4/3) \pi R^3 \Delta P + 4\pi R^2 \gamma$$

where the first volumetric term represents a reduction in free energy upon formation of a spherical bubble, and the second surface area term represents an increase in free energy as energy must be expended to form the new surface associated with the spherical bubble. ΔG varies with R and goes through a maximum at the critical radius R^* ($= 2\gamma/\Delta P$) defining the threshold free energy ΔG^* ($= 16\pi \gamma^3/(3\Delta P^2)$). Nuclei with radius smaller than the critical radius R^* re-dissolve, but those that are larger overcome the threshold free energy for nucleation ΔG^* and grow. Interfacial tension (γ) and pressure quench (ΔP) that is imposed thus play an important role in the process. The pressure quench is sometimes considered as the pressure drop used to induce nucleation. The significance of ΔP and the consequences of its different interpretations on the rate of nucleation has been addressed in the literature [25].

The rate of homogeneous nucleation (N_{hom}) depends on not only the energy barrier that must be overcome but also on the concentration of the gas molecules (C_0) as $N_{hom} \sim C_0 \exp [-\Delta G_{hom}^*/k_B T]$ where k_B is the Boltzmann constant and T is the temperature. Increasing the initial CO_2 concentration by incorporation of CO_2 -philic components (as in the case of block copolymers) thus would increase the number of nucleation sites in the polymer matrix. Increasing ΔP , that is foaming from higher pressures, will also lower ΔG_{hom}^* and lead to higher nucleation rates.

Another mechanism to lower the threshold energy barrier and increase the nucleation rate is to introduce nucleating agents and change the mode of nucleation from homogeneous to heterogeneous nucleation. Then, the threshold energy becomes $\Delta G_{het}^* = \Delta G_{hom}^* [S(\theta)]$. Here, the factor $S(\theta)$, which assumes values between 0 and 1.0, incorporates the effect of the contact angle θ between the bubble and the surface of the nucleating agent.

There are other factors that can also contribute and alter the Gibbs free energy. For example, if the polymer-gas solution is not in a quiescent state, applied stress influences the nucleation process. Nucleation is retarded under compressive stresses [88] but favored under shear [89] or tensile stress (as in elongation) [88].

Despite its generality, the classical nucleation theory (CNT) is often found unsatisfactory at the quantitative level. CNT can even fail to capture some qualitative features, such as the role of metastable, intermediate phases in the nucleation of stable phases. In gas foaming, where highly compressible fluids such as CO_2 in the vicinity of their T_c are utilized, interplays between liquid-vapor transitions and liquid-liquid phase separations become plausible [90]. To address such issues, alternative approaches involving computer simulations or density functional theory have emerged. For example, calculations using

density functional theory points out that the nucleated phase (bubble) may be either in the vapor or in the liquid state, with their corresponding energy barrier differences [90]. These approaches are however still at their early stage of development and there are difficulties in direct verifications of the predictions.

As nucleating agents, nanometric fillers such as carbon nanotubes, nanoclays and graphene are gaining increased attention [6,8]. At similar loading levels, compared to microparticles, nanometric additive particles provide greater number of nucleating sites per unit volume. There is however disagreement on the efficiency of nanofillers in foaming, with numerous counter-examples of their nucleating efficiency having been cited [91]. As a matter of fact, the number of nucleated cells is found to be always orders of magnitude less than expected. The mismatch is generally attributed to dispersion problems, evidenced by the presence of aggregates, as well as specific polymer/nanoparticle interactions.

A profound understanding of (a) the nucleating mechanisms, (b) the interaction among the particles and the polymer in presence of the blowing agent, (c) the concurrent nucleation phenomena of polymer crystals or other phases, and (d) how the particle shape, size, the nature of surface treatments affect nucleation is still missing, although representing opportunities for foam design and improvements in the future.

3.11. Modeling

Modeling the sequence of operations involved in the gas foaming technology is critical to designing processes aimed at achieving a desired foam density and morphology. As these systems are complex, it is not possible to use a single simple model. Different models are used for different stages that must however be interlinked [92–94]. A major weakness resides in the absence of reliable constitutive equations that can adequately describe the properties of the expanding polymer/gas solution undergoing foaming. The effect of CO_2 or other blowing agents on polymer viscosity, surface tension, mutual diffusivity and specific volume must be determined with great accuracy, and the constitutive equations must account for and describe their variations [95,96]. As a specific example, a rheological property of major interest in foaming is the biaxial extensional viscoelasticity of the polymer + CO_2 system at large deformations (in the non-linear regime) at high pressures. At present, there is no instrumental technique or theoretical model to address this important rheological question. Even though some measurement techniques and reliable models are available for the interfacial energy [41,43] between CO_2 and the polymer + CO_2 solution there are complications associated with the curvature of the interface, which, in foaming systems tend to be quite large [97]. Several papers addressed this issue from the molecular modeling point of view, with however no possibility to experimentally verify the model. As discussed earlier, there is also a need for an advanced nucleation phenomenon model. Among the various published work on modeling, it is worth of note the work by Taki [93], which in lieu of a practical nucleation model, employs experimental nucleation results to extrapolate and predict other cases. For modeling of the latest stage of growth, Tammaro et al. [49] developed a model to predict the cell wall morphology (and the extent of open/closed cells) by the effect of polymer viscoelasticity on cell wall retraction subsequent to its rupture. The model simulates numerically the bubble growth and impingement. However, the model does not directly address bubble nucleation. *In fact, as nucleation drives the whole foam evolution, the current lack of its full understanding presents the main actual limitation to modeling the foaming process.*

4. Future directions

Fig. 7 provides a summary of the topical areas discussed in this manuscript. Further advances in generating reliable data that will further advance our understanding of the nucleation phenomena, bubble growth and dynamics that may lead to bubble impingement and

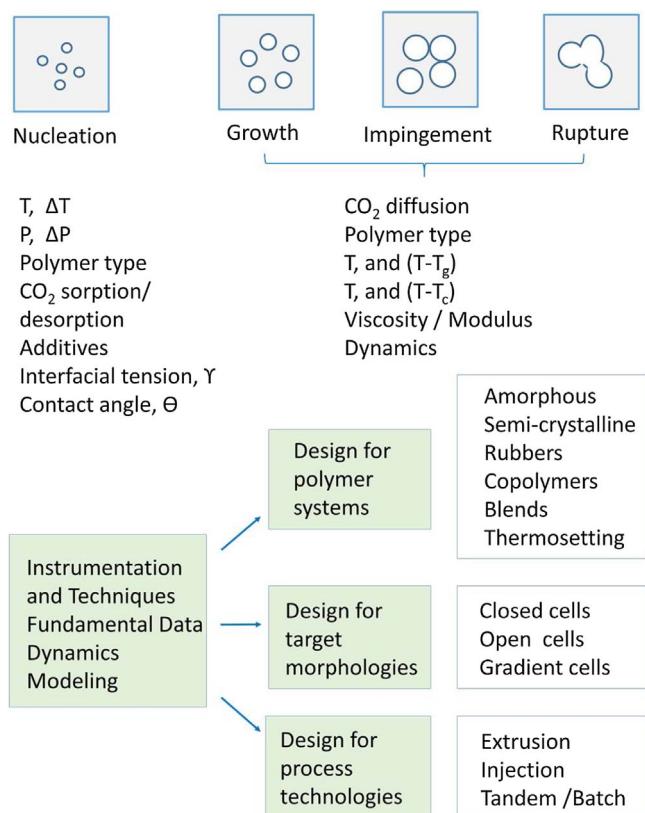


Fig. 7. Overview of the foaming process dynamics and impact of advances in generating fundamental data on equilibrium properties and dynamics along with modeling of various stages on the design for specific polymers, morphologies and process technologies in the future.

rupture that ultimately affect the pore morphology will bring the CO_2 -based foaming technology to a greater level of readiness for implementation. New instrumentation and techniques, and advanced models to assess the level of CO_2 sorption and desorption dynamics and how these concurrently alter the polymer properties such as the glass transition temperature, melting temperature (in semicrystalline polymers), viscosity and modulus will make a huge impact in future developments of new methodologies that may be scaled for continuous operations that are required for industrial implementation. In terms of polymer types, even though majority of past efforts has been on foaming of amorphous-glassy polymers, we anticipate a higher level of activity in foaming of semi-crystalline polymers, rubbery materials (with $T_g <$ room temperature), copolymers, polymer blends and composites. A special growth area will be thermosetting polymers. Efforts are expected to continue and grow in the areas of nano-porous materials, and systems that incorporate nanoparticles, as well as systems that display gradient porous morphologies.

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