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Publisher's version / Version de l'éditeur:

Cellular Polymers, 25, 4, pp. 199-220, 2006-07-24

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Supercritical Fluids in Thermoplastics Foaming: Facts or Fallacies?

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Received: 25 May 2006 Accepted: 24 July 2006

ABSTRACT

The past two decades have seen extensive interests and efforts for developing processes based on supercritical fluids (SCF). Microcellular foaming is one of these processes that take advantage of the unique properties of supercritical fluids when they are used as physical foaming agents (PFA). In this technology, the emphasis has been mostly focused on inert gases such as carbon dioxide and nitrogen that both inherently provides very high cell densities and very small cell sizes. Incidentally the benign carbon dioxide is frequently considered as the panacea of PFA, in response notably to the environmental pressures related to the destruction of the ozone layer. Hydrofluorocarbons (HFCs) have also been identified as potential alternative agents for extruded polystyrene foam. Unfortunately, HFCs remain difficult to process at the high concentrations required to yield low-density foams.

Surprisingly, the processing difficulties occur when the pressures required for dissolving high HFCs concentrations reach the range located immediately above the critical pressure of the PFA used. PS/HFC systems have been well documented in terms of abnormal behaviors occurring as the foaming agent gets into the supercritical conditions, and similar observations have also been made for other SCF used for thermoplastic foaming. These observations are reported here, and attempts are made to link the supercritical nature of the fluid to the PFA heterogeneities suspected under these conditions.

INTRODUCTION

Polymer processing involving supercritical fluids (SCF) has become very popular over the last twenty years. Processes such as polymer purification and fractionation, formation of nanoparticles or fibers, polymer polymerization and

microcellular foaming are widely documented in the literature⁽¹⁾. Supercritical carbon dioxide (CO₂), a benign substance that have drawn considerable attention in environmental debates, is frequently considered as the panacea of physical foaming agents. CO₂ exhibits a zero ozone depletion potential (ODP) as well as - compared to other PFA alternatives - a low global warming potential (GWP), it has a inherent ability to provide very high cell densities and it is inexpensive.

Unfortunately, while the kinetics of pressure-induced phase separation of a polymer in SCF is well documented in terms of the binodal and spinodal envelopes of the phase diagram⁽²⁾, the opposite, i.e. phase-separation of a SCF in a polymer is considered to follow basically classical nucleation mechanisms. This paradigm might need to be revisited, as many experimental facts involving supercritical conditions are left unexplained through classical approaches. Foaming with supercritical fluids may also present some drawbacks that have not yet been fully underlined. The purpose of this paper is to highlight the specific nature of some SCF dissolved in thermoplastics for foaming purposes through several key observations. Experimental facts support the idea that lack of homogeneous dissolution at a molecular level of the foaming agent may prevail when it is processed close to or over its critical point. Particular attention will be paid to extrusion foaming of polystyrene (PS) with hydrofluorocarbons (HFCs), these latter being identified as potential replacement for the ozone-depleting HCFC actually under their phasing-out stage. Moreover, illustrations on the addition of co-foaming agents to hard-to-process HFCs will be provided. This latter method is a convenient way to circumvent the negative issues related to PFA supercritical state in the extrusion-foaming process.

SUPERCritical FLUIDS: BASIC DEFINITIONS

The concept of a critical temperature was originally introduced by Johannes van der Waals in 1873 when he presented his doctoral thesis, entitled “*On the continuity of the liquid and gaseous states*”, to the University of Leiden in the Netherlands⁽³⁾. Only below this critical temperature that a gas can be condensed into a two-phase system composed of vapor and liquid, while above it, a fluid should remain homogeneous regardless of the applied pressure. The critical locus is located on “top” of the vapor pressure curve, where are also defined an associated critical pressure and a critical volume. Accordingly, the supercritical state was by definition associated to the P-T region located above the critical temperature and critical pressure, with the critical locus corresponding to the disappearance of the meniscus separating the vapor and liquid phases (see Figure 1).

Figure 1. Reduced Pressure-Volume diagram, showing isotherms. Features from supercritical state are also shown (adapted from Ref.⁽²³⁾), as well as processing conditions for various polymer/PFA systems

A few years after van der Waals dissertation, Hannay and Hogarth reported the tunable dissolving power of supercritical fluids during a meeting of the Royal Society in London in 1879⁽³⁾. This observation took almost a century to get fully appreciated and technically exploited, especially using carbon dioxide. However, the technologically attractive adjustable solvation efficiency of SCF is only achievable with highly compressible fluids or, stated differently, fluids with density finely tunable through very small variations in pressure. Such a behavior only occurs in pressures and temperatures close to the critical conditions. Thus, the useful behavior of supercritical fluids lies in a very small area of the supercritical state region, and even if the fluid is processed above its critical P and critical T, very high pressure and/or temperature could make the fluid to behave simply as a near perfect gas or as a common liquid. So the claimed specific properties usually associated to SCF, such as low viscosity, high isothermal compressibility and large diffusivity, are mostly restricted to a much smaller set of conditions.

In order to reflect these subtle but important distinctions and to highlight their valuable features, new definitions for supercritical fluids have been recently

introduced: “Supercritical fluids are gases at pressure and temperature *SLIGHTLY* above those of the vapor-liquid critical point”⁽⁴⁾ or “a supercritical fluid is defined as any fluid which is at a temperature greater than its critical temperature T_c , regardless of the pressure or density”⁽⁵⁾.

SUPERCritical FLUIDS AND FOAMING: HISTORICAL PERSPECTIVES

The introduction of SCF as foaming agent has followed two different paths. First, supercritical fluids have been early associated with the development of the microcellular foaming technology. The technology developed led to foams with very high cell densities, in the order of 10^9 cell/cm³ of unfoamed polymer, combined to very small cells, typically less than 10 microns. Second, because of environmental regulations gradually forcing the industry to adopt ozone-friendly foaming agents, HFCs have been widely investigated as potential replacements. Unfortunately, HFCs are much less soluble in polystyrene than the formerly used CFCs and soon-to-be-banned HCFCs. Consequently, the pressures required to dissolve the required PFA content combined with the processing window of polystyrene foam made these new PFAs to be injected and processed under supercritical state.

Microcellular Foaming

Interestingly, one of the first patent on microcellular foaming issued in 1984, “*Microcellular closed cell foams and their method of manufacture*”⁽⁶⁾, had no mention at all on the specific use of supercritical fluids. In an enhanced version published eight years later, “*Microcellular thermoplastic foamed with supercritical fluid*”⁽⁷⁾ the authors claimed several improvements, i.e. an increased number of cells nucleated as well as smaller cell sizes, through the use of a supercritical fluid instead of a foaming agent in a gaseous state. Use of SCF is usually associated to enhanced solubility and diffusivity in the polymer matrix, which makes the dissolution process faster: “*the liquid-like solubility and gas-like diffusivity make it possible to dissolve sufficient CO₂ in a polymer quickly*”⁽⁸⁾. Since then, microcellular foaming has been intimately linked to supercritical fluids, essentially carbon dioxide or nitrogen, although the prerequisites remain a high level of saturation of the foaming agent and a rapid pressure drop⁽⁹⁾. Obviously, due to the inherently low solubility of CO₂ or N₂ in most common polymers, and since the processing temperature lies usually well above the critical temperature of the fluid, high pressures are required to obtain large PFA contents (“*Preferably, the weight ratio of supercritical fluid to polymer should typically be about 10%, or greater*”⁽¹⁰⁾).

The combination of these conditions makes the processing window to be obviously located in the supercritical zone. Interestingly, ultramicrocellular foams (cell size less than 1 micron and cell density greater than 10^{12} cells/cm³) have been reported for the PMMA/CO₂ system, with the carbon dioxide in its SUB-critical state⁽¹¹⁾. In this specific system, the strong affinity between CO₂ and PMMA enables the dissolution of the large gas concentration required for high cell nucleation densities and small cell size at pressure and temperature well below the critical conditions.

From CFCs to HFCs

In response to the Montreal Protocol (1989), the foam industry has moved steadily from “easy-to-process” physical foaming agents such as CFCs, to less soluble but more environment-friendly components. Powerful ozone depletion substances commonly used by foam producers (CFCs) were then gradually replaced by hydrocarbons (for non-insulating purposes) and HCFCs (such as HCFC-142b, for insulation applications). Note that HCFCs are only being considered as transitory replacements because of their small but non-negligible ozone-depleting potential.

Among the different chemicals potentially useful for insulating foam manufacturing purposes, 1,1,1,2-tetrafluoroethane (HFC-134a) was recognized as one of the best candidates commercially available. “*At this date, the most viable non-ozone depleting alternatives for the XPS (extruded PS foams) industry are HFC-134a and CO₂ or blends thereof*”⁽¹²⁾. Focusing on long term performance, HFC-134a would be the preferred choice over carbon dioxide, considering its intrinsic low thermal conductivity and slow diffusivity, with values very close to HCFC-142b⁽¹³⁾.

Although HFC-134a and HCFC-142b exhibit similar molecular weights and critical parameters P_c and T_c (see Table 1), HFC-134a is far less soluble in PS and its processing for foam extrusion is problematic at high concentrations. At a low content, i.e. 6 wt.%, a nice foam can be easily achieved with a density of 49 kg/m³ and an adequate morphology, as shown in Figure 2a. However, increasing HFC-134a content above 7.5 wt.% for reducing density in the 40 kg/m³ range or lower makes the process unstable and leads to foams with unacceptable morphology: large holes, in the order of a few millimeters (typically named “blow holes”) coexist with a microcellular morphology, as shown in Figure 2c⁽¹⁴⁾.

The concentration threshold at which difficulties occur is approximately 7.5 wt.%, and is usually referred as the “limiting solubility” of HFC-134a,

Table 1. Selected physical properties of some blowing agents

	HCFC-142b	HFC-134a	HFC-152a	HFC-245fa	CO₂
Formula	CH ₃ CF ₂ Cl	CF ₃ CFH ₂	CH ₃ CHF ₂	CF ₃ CH ₂ CHF ₂	CO ₂
Molecular weight (g/mol)	100.5	102.3	66.1	134.0	44.01
Boiling point (°C)	-9.6	-26.4	-24.7	15.3	-78.45
Critical temperature (°C)	136.85	101.3	113.5	157.5	31.05
Critical pressure (MPa)	4.15	4.06	4.58	3.623	7.38
λ_{gas} (mW/m.K) @ 25 °C	11.5	13.6	13	12.2	16.6
ODP	0.066	0	0	0	0
GWP _{100 yr}	2000	1300	140	820	1

although this designation here has no thermodynamic meaning and relates essentially to processing issues. As HFC-134a content gets closer to this limit, high cell densities (10^9 cells/cm³⁽¹⁵⁾) are easily achieved without any nucleating agent, as shown in Figure 2b. The pressure associated with this critical concentration is roughly 4 MPa, close then to the critical pressure of HFC-134a (4.06 MPa). The processing temperature was always above HFC-134a critical temperature (101 °C). On the opposite, HCFC-142b is highly soluble in PS and dissolution of 11 wt.% of HCFC-142b only requires 2 MPa, thus well below its own critical pressure. Large cells are usually obtained and use of nucleating agent is mandatory.

MORE ON HETEROGENEITIES WITH SCF

Presence of blow holes in foams processed with excess of HFC-134a above the said critical limit is not the only anomalous evidence related to PFA supercritical behavior. Rheological data and phase separation (solubility) measurements also provide additional support of the strange nature of this fluid above a threshold concentration-pressure. Moreover, HFC-134a shares some of its “anomalies” with other HFC, such as HFC-245fa⁽¹⁶⁾ and HFC-152a. These latter HFCs also have their critical P and T parameters located in the processing window of interest (see Table 1).

Figure 2. Foams made of PS and HFC-134a: From top to bottom: (a) 6 wt.% HFC-134a; (b) 7.1 wt.% HFC-134a; (c) 8 wt.% HFC-134a

Viscosity Behavior

The plasticization induced by the PFA on PS can be assessed through on-line viscosity measurements, and typical results obtained for either HFC-134a or HFC-152a indicate a linear trend when the viscosity reduction is plotted on a logarithmic scale as a function of the PFA content, as shown in Figure 3. This linear dependency prevails up to the said critical concentration, roughly 7.5 wt.% for HFC-134a and 6.5 wt.% for HFC-152a. Above this concentration, the viscosity depression is severely reduced and is almost inexistent in the specific case of HFC-134a. The behavior observed suggests that part of the additional PFA exceeding the critical concentration no longer contribute to the plasticization effect as individuals. The undissolved PFA molecules then tend to form localized clusters due to strong interactions existing in the supercritical state.

Effect of hydrostatic pressure on the viscosity has been also investigated for HFC-134a. As reported in Ref.⁽¹⁷⁾, an increase in pressure yields a small but

Figure 3. Viscosity reduction for mixtures of PS/HFC-134a (180 °C) and PS/HFC-152a (155 °C), as determined from viscosity measured at constant stress. Arrows indicate concentration threshold for each mixture

significant increase in viscosity, which is the expected behavior for a single-phase polymer melt. In contrast, in systems involving PFA content beyond the threshold concentration, an increase of the hydrostatic pressure leads to a modest lowering of the viscosity, as displayed in Figure 4, suggesting additional dissolution of a rather small portion of the “extra” fluid injected (“extra” meaning the fraction in excess of the said critical concentration). However, in comparison to the level of plasticization observed at smaller HFC-134a content, the additional plasticization induced from increasing the pressure remains relatively small, and the reduction of the foaming agent efficiency, in terms of plasticization, still prevailed at high hydrostatic pressures.

Reduction of the foaming agent efficiency was also suggested in another, yet theoretical, study. Application of the Simha-Somcynski lattice-hole theory using the equation of state properties of the components used in foam extrusion was attempted for mixtures of PS and either HCFC-142b, HFC-134a or CO_2 ⁽¹⁸⁾. The introduction of an efficiency factor κ was needed to take into account discrepancies between the model predictions and experimental constant-stress viscosity results. This factor implied that only a portion of the PFA was effective in the plasticization process and the authors suggested that either a leakage or an incomplete dissolution of the foaming agent explained the divergence

Figure 4. Effect of pressure on shear viscosity for two different mixtures of PS and HFC-134a (viscosity measured at constant stress, 40 kPa)

between the experimental data and the computed results. Retroactively, it is interesting to note that computed κ factors for HCFC-142b (~ 1), CO₂ (0.77) and HFC-134a (0.58) are reflecting the nature of the fluids in the conditions used during the extrusion experiments: the smaller the κ factor, the closer the system was to its supercritical locus.

Phase Separation and Solubility

A novel ultrasonic technique has been used in several occasions to investigate different stages of foam extrusion, from plasticization to bubble growth⁽¹⁹⁾. This technique is particularly sensitive to the presence of a second phase, and bubbles can be easily detected through the decrease of the magnitude of the ultrasonic signal (increasing attenuation). The pressures at which phase separation occurs, i.e., the degassing pressures, could be linked to the equilibrium solubility as measured using off-line methods, and fair agreement have been previously reported for various polymer-PFA systems. This is illustrated in Figure 5a for HFC-152a in PS where comparison is made between degassing pressures obtained with the ultrasonic technique and off-line solubility data using a magnetic suspension balance⁽²⁰⁾. Unexpectedly, for some PFA types, the degassing results have been found to deviate at high PFA concentrations from the anticipated linear Henry-law dependency, with higher-than-expected degassing pressures recorded. This is shown also in Figure 5 for three different HFC dissolved in polystyrene, with the departure from the linear trend localized close to the critical pressure of the fluid.

Inadequate dissolution has been suspected in the case of HFC-245fa, with the lack of a homogeneous phase prior to the degassing step, as detected with the ultrasonic probes⁽¹⁶⁾. As shown in Figure 6, erratic fluctuation on attenuation is present at high HFC contents, and this could be associated with the presence of heterogeneities in the melt.

These “solubility discrepancies” are not only restricted to HFCs, and abnormal/unexpected results have also been reported for n-pentane⁽²¹⁾. This hydrocarbon, a standard foaming agent for many polymers, is not frequently considered as a supercritical fluid because of its relatively high critical temperature (196.5 °C). However, because of the elevated temperatures involved in the extrusion of polycarbonate (PC), the processing window was such that it brought the pentane into the supercritical state. Similar discontinuities as those reported for HFC are observed at the critical pressure border (Figure 9 of Ref.⁽²¹⁾). Incidentally, the foams extruded under these conditions exhibited a huge increase in their cell nucleation densities, with levels typical of microcellular foams (10^{10} - 10^{12} cells/cm³)⁽²¹⁾.

Figure 5. (a) Top; degassing pressures for HFC-152a in PS (measured at 155 °C), compared to solubility data, excerpted from Ref.⁽²⁰⁾. (b) Bottom; degassing pressures for HFC-245fa (190 °C) and HFC-134a (180 °C) in PS. This latter is compared to a mixture of HFC-134a (8 wt.%) and ethanol (1.35 wt.%)

Figure 6. Noise in the attenuation of the ultrasonic signals as recorded for different levels of HFC-245fa in PS, with pressure maintained above 10 MPa and temperature set to 190 °C (graphs excerpted from Ref.⁽¹⁶⁾)

Nucleation issues can also be highlighted through the following examples involving PS foam extrusion with HFC-152a. Concentration of the HFC was set to 8.1 wt.%, with the corresponding pressure required for adequate dissolution lying close to the critical pressure of the PFA (see Table 1 and Figure 5a). As shown in Figure 7, fine cells prevailed as the foaming temperature was maintained above 120 °C, and a sudden morphology change occurred as the processing temperature was lowered close to the critical temperature of HFC-152a (113.5 °C).

Density Inhomogeneities in SCF and SCF-Polymer Systems

Because no more phase separation exists in the critical region does not necessarily mean that the density of the fluid is homogeneous at a microscopic level. With the numerous development in technologies based on SCF, the supercritical state of neat fluids and mixtures of fluids has been widely investigated⁽²²⁾, with considerable attention being also paid to polymer solutions involving the SCF as the solvent. It has been demonstrated from experimental, theoretical and computational studies that local density inhomogeneities do really exist in SCF⁽⁵⁾. It has also been proposed that the strong manifestation of the attractive forces could even lead to a percolated system at low temperature and high density, in contrast to the isolated small clusters expected at high temperatures and low densities (Figure 1)⁽²³⁾. Unfortunately, the foaming practices rely on the opposite compositions with the SCF being the minor phase. Transition between

Figure 7. Different cellular morphologies for PS foamed with 8.1 wt. % of HFC-152a, as the temperature is decreased toward the critical temperature of HFC-152a (113.5 °C). Please note that the scale is identical for all three micrographs

the critical state prevailing in the PFA before its dissolution into the polymer, with possible presence of density gradients and clusters of fluid molecules, to its behavior within the macromolecular network of the host resin remains unclear. Knowledge is still to be built on that specific issue, but hypotheses could be proposed based on current science of SCF.

Recently reviewed by Tucker⁽⁵⁾, the issues of density inhomogeneities in supercritical fluids are of primary importance in the development of new chemical processes based on control of solvation properties. For many of these applications, the SCF acts as the solvent (major phase) in which solutes, such as polymers, are dissolved or precipitated. As mentioned above, density inhomogeneities do exist in pure fluids close to their critical points, but computer simulations and experimental data on various fluids (methane, ethane, CO₂) have demonstrated that the magnitude of this effect is rather small, and lies around 20%⁽²⁴⁾. However, it has been shown that in dilute supercritical solutions, i.e. with the addition of a very low concentration of polymer in the SCF solvent, density inhomogeneities are amplified and can be two or three times greater than that of the bulk fluid⁽²⁴⁾. In addition, the magnitude of this increase should correlate with the free energy of the solute-solvent interaction, thus indicating that the primary determinant of the extent of density variations is the relative attraction between the solute and the solvent. This particular behavior may be seen as a liquid-like condensation of the fluid molecules around the dissolved polymer. Under such specific supercritical conditions, the attractive solute-solvent interaction would be greater than that between the solvent molecules. According to Urdahl *et al.*⁽²⁵⁾, interactions between the solvent and the solute decrease very rapidly with the increasing distance: “*a localized phase transition could occur forming a nanodroplet composed of only two or three solvent shells*”. Interestingly, these authors underlined that these stable structures do not change over a range of density of the solvent. It is easy to foresee these nanodroplets as highly efficient cell nucleation sites during the foam nucleation stage.

SUPERCritical FLUIDS AND PHASE SEPARATION MECHANISMS

Results displayed in Ref.⁽²⁶⁾ on foaming of polypropylene (PP) with either isopentane or CO₂ will serve to evidence the particular nature of “nucleation” for fluids of different natures. Low cell density levels (10²-10⁶ cells/cm³) were reported for sub-critical conditions (low content of CO₂ and isopentane, this latter being always processed at T below its critical temperature of 187 °C). Under these processing conditions, the system was still very sensitive to the

presence of a nucleating agent, which increased the cell density by several decades in many cases. As shown in Figure 8, when the content of carbon dioxide was raised to 5 wt.%, with corresponding equilibrium solubility pressures⁽²⁷⁾ greater than 7 MPa (supercritical state), cell density reached 10^8 cell/cm³, and remained practically insensitive to the addition of talc as the nucleating agent, contrarily to sub-critical conditions where large nucleation enhancement always occurred upon talc addition. Phase separation at high CO₂ content in presence of talc thus did not follow classical nucleation rules where the lower activation energy barrier of heterogeneous nucleation eases the nuclei formation. Similar trends were also observed for the PS/HFC-134a system, investigated at various PFA and nucleating agent contents⁽²⁸⁾. In this study, degassing pressures, determined using the above-mentioned ultrasonic technique, appeared to be modified by the presence of talc only for sub-critical concentrations of PFA (Figure 4 of Ref.⁽²⁸⁾). It has been previously proposed that the increase of the degassing pressure with addition of nucleating agent may be the consequence of PFA concentration gradient induced by the presence of solid particles⁽²⁹⁾. Here again, PFA inhomogeneities throughout the polymer matrix were suspected to explain the early onset of phase separation.

Figure 8. Cell density in PP foamed with CO₂, with various contents of talc (excerpted from Ref.⁽²⁶⁾). The dotted arrow close to 4.5 wt.% corresponds to a solubility pressure of approximately 7.1 MPa (critical pressure of CO₂), according to published solubility data⁽²⁷⁾

Although the classical homogeneous nucleation and growth mechanism is generally accepted for thermoplastic foaming, many discrepancies between theory and experiments reported over the years in literature justified the need to look for an alternative process. Stafford and co-workers suggested as a possible phase separation mechanism the spinodal decomposition followed by coarsening, with concentration fluctuations inherent to this mode of phase separation⁽³⁰⁾. The nonclassical nucleation theory of spinodal decomposition was pioneered by Cahn and Hilliard, in the late fifties. However the first to christen the “spinodal” was in fact van der Waals in his doctoral thesis, who has proposed this alternate nucleation process based on diffusion from a parent phase⁽³⁾. Contrarily to the nucleation and growth mechanism where droplets grow through a downhill diffusion process (diffusion from high to low concentrations), coarsening occurs during the spinodal decomposition through uphill diffusion. While the spinodal decomposition mechanism is well characterized and thus widely accepted for phase separation of polymer dissolved in supercritical fluids (see for instance Ref.⁽²⁾), literature is very scarce on this possible occurrence when it comes to thermoplastic foams. A theoretical study on the subject using the Sanchez-Lacombe theory has been published with emphasis on the fact that spinodal decomposition could not reasonably happen for systems like PS/CO₂, PS/N₂ and PP/CO₂, although possibility could still exist for other systems⁽³¹⁾. In the same study, using classical nucleation theory, the authors failed to explain the high nucleation rates observed during batch foaming experiments of PVC charged with 7.5 wt.% of CO₂ for temperatures higher than 85 °C. Surprisingly the saturation pressures associated with these conditions (Table II of Ref.⁽³¹⁾) would fall slightly above the critical pressure of carbon dioxide.

Another strange coincidence relating particular foaming behavior with the supercritical region has been recently reported on extrusion foaming of poly(lactic acid) (PLA) with carbon dioxide⁽³²⁾. As displayed in Figure 9, a drastic increase in the cell density, accompanied by an abrupt foam density reduction, occurred at a CO₂ concentration of approximately 7 wt.%, which corresponds to a pressure of 7 MPa based on equilibrium solubility measurements⁽³³⁾. Once more, it was reported that the effect of a nucleating agent, beneficial at lower PFA concentrations, ceased to contribute significantly at that critical concentration.

MIXTURES OF FOAMING AGENTS: ALLEVIATING THE CRITICAL ISSUE?

With the growing interest in supercritical fluids for their modulated solvency power, it is not surprising to find that the SCF engineering science has

Figure 9. Cell density in PLA foamed with CO₂, with and without talc (excerpted from Ref.⁽³²⁾). The dotted arrow close to 7 wt. % corresponds to a solubility pressure of approximately 7.1 MPa (critical pressure of CO₂), according to published solubility data⁽³³⁾

also explored the thermodynamics of mixtures of fluids. The impact of the composition on the tuning of the critical point as well as the specific properties inherent to the supercritical region is well documented. Literature is abundant on mixtures based on CO₂, since carbon dioxide remains one of the prime candidates in SCF applications. Critical T_c and P_c point shifting are reported with respect to the composition of the binary mixture, the co-agent being frequently an alcohol or a hydrocarbon⁽²²⁾. Positive deviations from linear additivity rule are frequently observed with respect to the critical pressure, and this synergistic effect, sensitive to the molecular weight of the co-agent would be anticipated to be beneficial to the case of hard-to-process PFA such as HFC-134a, by shifting the critical pressure to a value well above the pressure needed to dissolve the required amount of gas at a molecular level.

Use of mixtures of physical foaming agents in thermoplastic foam extrusion has been an industrial practice for a long time. It has been reported in the patent literature that use of a co-agent such as a hydrocarbon or an alcohol with the unstable HFC-134a can favorably modify the processing conditions (examples are provided in Refs.⁽³⁴⁾ and ⁽³⁵⁾ for cyclopentane and ethanol, respectively).

This last specific case, HFC-134a with ethanol, is illustrated in Figure 10 and Table 2. PS was successfully foamed using a high concentration of HFC-134a (8 wt.%), through the addition of a small fraction of ethanol (1.35 wt.%). This system has been extensively investigated with respect to the conditions that yield phase separation (degassing pressures) during the extrusion of low-density foams. Several key observations should be reported here:

- The premature nucleation previously reported in terms of high degassing pressures, associated with the hypothetical presence of PFA clusters acting as pre-nuclei, was reduced with resulting degassing pressures that almost obey the same Henry-law constant determined from lower PFA concentrations (see Figure 5b). It should be noted that for mixtures of low and high volatile components, the observed degassing pressures have always been essentially controlled by the substance having the higher volatility⁽³⁶⁾.
- As displayed in Figure 10, a stable and adequate morphology, similar to that obtained with sub-critical gases (HCFC-142b for instance), could be achieved, with the elimination of the undesired blow holes.
- The co-agent has its own plasticization efficiency, and that could be detrimental to the process through over-plasticization as indicated in Table 2 for high content of ethanol. Moderate use of the co-agent is thus mandatory.

Table 2. Characteristics of PS foams made with mixtures of HFC-134a and ethanol ⁽¹⁴⁾

Blowing agent (wt.%)		Foam density (kg/m ³)	Cell diameter (μm)	Open cell content (% vol)
HFC-134a	Ethanol			
6	0	49	180	Good
7	0	40-48	N/A	Blow holes
6	1	48	290	Good
6	2.3	42	330	<5%
6	5	Run aborted: overplasticization		
8	1.35	40	<100	<5%

Figure 10. Morphology of the foam produced with 8 wt. % HFC-134a /1.35 wt. % ethanol⁽¹⁴⁾

CONCLUSIONS

While the classical nucleation theory, i.e. nucleation and growth, appears to be well suited for sub-critical systems, many experimental facts that involve PFA processed near its supercritical conditions cannot be easily explained by these classical mechanisms. Lack of solubility and incomplete dissolution of the HFC are routinely invoked when it comes to explain the processing difficulties occurring with concentrations in the neighborhood of the supercritical region. Surprisingly, these explanations go against the main claims usually associated to SCF, i.e. high solubility and fast diffusion.

The experimental observations previously reported may support the hypothesis that a homogeneous one-phase system is not achieved at a molecular level under these supercritical conditions. While the processing conditions involved with carbon dioxide are usually well above its critical temperature, some HFC identified as potential alternative foaming agents are being processed under conditions that match closely the critical locus. The scenario of premature clustering is then appealing considering the density inhomogeneity reported in supercritical fluids, as well as that hypothesized for systems using nucleating agents. Nevertheless, spinodal decomposition or a similar mechanism is still attractive and could obviously prevail for foaming agents in the supercritical state.

The present work also suggests potential explanations for the mechanisms associated to the benefits obtained when using mixtures of foaming agent, the claimed improvements being already part of the patent literature for extruded low-density PS foams. The tuning of the critical locus would be included in the actual research pathways, which aim at identifying suitable co-agents and adequate concentrations, in order to eliminate efficiently the processing instabilities associated with the high HFC content, while maintaining short/long terms properties of the resulting foam.

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