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Heterogeneous Nucleation in Foams as Assessed by In-line Ultrasonic Measurements*

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ABSTRACT: The conditions prevailing during the nucleation stage of the thermoplastic foam extrusion process in which a physical foaming agent is involved are one of the key steps in the design and optimization of the process. The conditions that induce phase separation and bubble nucleation are obviously linked to the solubility parameters, i.e., temperature and pressure at a given foaming agent content, conditions that can be probed during degassing experiments. It has been reported that adding a nucleating agent can significantly modify these degassing conditions. An in-line detection method based on ultrasonic sensors has proven to be sensitive to the onset of the phase separation. This method was used to investigate the influence of both talc and foaming agent concentrations on the nucleation cell density and degassing conditions for polystyrene–HFC-134a mixtures. A qualitative model based on foaming agent concentration gradient near the nucleating agent particles is proposed.

KEY WORDS: thermoplastic foam, nucleation, talc, Gibbs free energy, surface tension.

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INTRODUCTION

Use of nucleating agents in the thermoplastic foam industry is a current practice. In addition to the generation of a fine and homogeneous cell structure, use of a small fraction of nucleating agent is also beneficial to density reduction. For example, under homogeneous nucleation conditions, polystyrene (PS) foamed with 10 wt% HCFC-142b yields a mean cell size of 1.82 mm and a foam density of 72 kg/m³. With the addition of only 1 wt% talc, the cell size drops to 119 µm and the density is reduced to 32 kg/m³ [1].

The classical homogeneous nucleation theory states that, with the polymer/physical foaming agent (PFA) system being in a metastable state (thermodynamic instability) resulting from the pressure drop, nucleation relies on the overcoming of an energy barrier in order to form viable nuclei [2]. This yields a stable two-phase system. A critical radius for the nuclei should then be reached before it would be energetically favorable for the nucleus to grow. The derivative of the Gibbs energy (Equation (1)), which opposes the volume free energy (volume effect) to the interfacial energy (surface effect), gives the minimum needed for the cluster radius (Equation (2)):

$$\Delta G_{\text{hom}} = -V_b \Delta P + A_{bp} \gamma_{bp} \quad (1)$$

$$r^* = \frac{2\gamma_{bp}}{\Delta P} \quad (2)$$

where, V_b is the volume of the nucleus, ΔP is the gas pressure in the bubble nucleus, A_{bp} is the surface area of the bubble, γ_{bp} is the surface energy of the polymer–bubble interface, and r^* is the critical radius.

Nucleation can also be heterogeneous, where the energy barrier is lowered through modification of the interface between the matrix and the new phase, usually through the addition of solid particles. Classical heterogeneous nucleation implies that the interfacial energy is reduced with the nuclei being formed at the interface between a liquid and the surface particle [2].

However, this classical model is not widely accepted in the thermoplastic foam area. Other mechanisms have been proposed. Gas absorption was observed to increase in filled polymers. This suggests that the blowing agent accumulates at the polymer–filler interface acting as nucleation sites [3]. These findings are however in contradiction with another study conducted with a magnetic suspension

balance on solubility of filled polymer system, which concluded the absence of either a positive or a negative effect on the gas sorption in the polymer [4]. Another proposed explanation is that nondissolved gas remains in micropores present on the surface of particles to enhance the nucleation [5]. A model based on preexisting microvoids has been proposed, and it was validated for autoclave microcellular foaming of polystyrene using rubber particles as the nucleating agent [6]. These voids resulted from the stress induced between the rubber and polystyrene phases due to their difference in thermal expansion coefficients.

The foam extrusion process however involves shear deformation, especially for the flow in the shaping die, which was found to amplify the effect of the nucleating agents. A cavity model has been proposed considering microcrevices at the nucleating agent surface as the primary initiators for cell nucleation [7]. Increasing the shear rate would generate higher stresses that would in turn circumvent the surface tension of the gas phase present in the cavities. Other works have paid attention to the importance of the specific surface of the nucleating agents [8] and that of the interaction of the polydispersity of the particle size with the saturation pressure [9]. Unfortunately, most of these models ignore the thermodynamics of the multiphase systems.

Our previous works, based on the use of an in-line noninvasive ultrasonic technique sensitive to the onset of bubble appearance during the nucleation stage, have clearly indicated that the presence of a nucleating agent increases the pressure at which phase separation occurs (reported in this paper as degassing pressure) [10]. The pressure increase was significantly larger for talc than for titanium dioxide particles, and the resulting pressures were comparable to those observed for homogeneous nucleation with an absolute increase of 2 wt% of blowing agent in the neat polymer. This suggested that the concentration of blowing agent was not uniform in the polymer matrix and was higher in domains close to the nucleating agent particles. This concentration should depend on the thermodynamic properties of the nucleating agent, in particular its surface energy. We concluded that these domains became nucleating sites as soon as the pressure reached the critical value corresponding to their higher concentration.

In the present work, we study the effect of both PFA concentration and nucleating agent content on the degassing pressure and cell density. We then propose a mechanism based on migration of PFA molecules that induces concentration gradients, in order to reduce the Gibbs free energy.

EXPERIMENTAL

Foam extrusion was carried out on a Leistritz 34 mm corotating twin-screw extruder equipped with an instrumented slit channel (pressure, temperature, and ultrasonic probes) as described in [10]. A gear pump was placed at the channel exit to allow controlling the pressure inside this channel. The foaming agent HFC-134a was injected in the extruder barrel using a preparative chromatography pump to maintain a constant concentration of PFA (set at two nominal levels, 3 and 6 wt%). The polystyrene was Novacor 1301 (MFI = 3.5 dg/min) from Nova Chemicals. The nominal flow rate was set at 5 kg/h. The talc used as nucleating agent was PolyTalc AG 445 from Specialty Minerals Inc., having a mean particle size of 5.5 μm and a specific surface of 9.5 m^2/g . The concentration of talc in the melt was set to incremental values of 0, 1, 2, and 3 wt%.

The investigated melt temperatures were 172 and 182°C. The pressure was high enough to prevent bubble nucleation in the slit channel. Prior to degassing trials, the shear stress prevailing within the slit was measured using three pressure transducers equally spaced and flushed, mounted at the inner surface of the channel. Measurements of the degassing conditions were carried out according to the procedure described in [10]. Foam specimens made with and without nucleating agents were then collected for morphology measurement and analysis.

RESULTS AND DISCUSSION

Degassing Pressures

First the degassing pressure results for the neat PS are compared to solubility data obtained from the literature. As shown in Figure 1, the pressure needed to maintain 3 wt% dissolved HFC-134a is approximately 2–2.2 MPa, and increases to 4–4.2 MPa for 6 wt% HFC-134a, in the 170–185°C range. Sato and coworkers reported for PS–HFC-134a static solubilities of 3.12 wt% at 150°C and 2.2 MPa, and 2.34 wt% at 200°C and 2.4 MPa [11], which is in fair agreement with our results. The small differences observed between the two sets of data could be imparted to various sources of uncertainty and experimental conditions: effect of flow, elastic recovery of the polymer matrix [12], etc.

Since solubility usually increases with lower temperatures, it may be surprising at first glance to obtain at 3 wt% HFC-134a, a set of degassing pressures for 172°C above that of 182°C. This could be explained by the impact of the rheological behavior of the resin as it flows through

Figure 1. Degassing pressures for different content of talc at two HFC-134a concentrations (circle: 3 wt%, square: 6 wt%) and two temperatures (open symbols: 172°C, closed symbols: 182°C).

the instrumented channel, as proposed in [12]. This results in a parabolic profile of the degassing pressures as a function of temperature, with the minimum of the curve being a function of the level of plasticization induced by the foaming agent. While at high temperatures the degassing pressure profile may match the static solubility behavior closely, lowering the temperature impacts the elastic rheological behavior, which eases the degassing conditions, thus yields higher pressures for the phase separation onset. This upward trend is shifted to much lower temperatures as the PFA content is increased, due to enhanced plasticization which also affects the overall rheological behavior.

As shown in Figure 1, for the experiments conducted with only 3 wt% HFC-134a, a huge increase in the degassing pressures is observed with the addition of 1 wt% talc. For example, the experiment conducted at 172°C exhibits an increase of 1.43 MPa, compared to the former degassing pressure of 2.21 MPa for the neat PS. However, the subsequent step increase of talc from 1 to 2 wt% yields no change in the degassing pressure. Surprisingly, use of 3 wt% talc induced even higher values that typically reached a level similar to those observed with 6 wt% HFC-134a.

With 6 wt% HFC-134a, the first increase of the degassing pressure with talc addition is moderate and remains in the 0.7 MPa range. This mild but still significant increase compares well with previous observations for the PS-HCFC-142b (10 wt%) system with talc as the nucleating agent [10]. For these cases, we can easily make the hypothesis that the increase of the degassing pressures comes from an increase of the foaming agent concentration in the neighborhood of the solid particles. Attempting this same explanation for the increase observed with 3 wt% HFC-134a/1 wt% talc would require a drastic relative increase in the PFA content near the particles, typically from 3 to 4.5 wt% or even higher, which is difficult to conceive in a first approach.

Nucleation Density and Cell Morphology

Cell nucleation densities β , i.e., the number of cells per cubic centimeter of unfoamed resin, were obtained from a quantitative analysis of micrographs of the foams (examples of foam morphologies are displayed in Figure 2) and computed according to the following equation:

$$\beta = \frac{6(\rho_{PS}/\rho_{foam} - 1)}{\pi d_{cell}^3} \quad (3)$$

The results, displayed in Figure 3, exhibit similar trends as those observed for the degassing pressures. It is obvious from this figure that the number of particles is not the sole parameter controlling the number of nucleating sites, since different levels of cell densities are associated with the two investigated PFA contents. As reported in [9], increasing the gas content may increase the efficiency of the smaller particles. This efficiency, based on the number of cells per unit particulate, can be approximated as 1:100 (cell per talc particles) for 3 wt% HFC-134a, and 1:30 for 6 wt% PFA.

The largest impact of the nucleating agent, i.e., switching from homogeneous to heterogeneous nucleation, was obtained with 1 wt% talc and 3 wt% HFC-134a. For all other cases, even in the case of 3 wt% talc at 172°C that yielded abnormally high degassing pressures, a small but steady increase of the cell nucleation density is obtained through an increase of the talc content. This steady increase from 1 to 3 wt% talc is roughly the same for any of the investigated conditions, and can be estimated as 4×10^5 cell/cm³/wt% of talc, or stated differently, the addition of talc beyond 1 wt% would provide a modest increase of the efficiency by one cell per 300 talc particles.

Figure 2. Micrographs of foams produced at 172°C , for various contents of HFC-134a and talc. Magnification is the same for all micrographs. (a) 6 wt% HFC-134a, no talc; (b) 6 wt% HFC-134a, 1 wt% talc; (c) 6 wt% HFC-134a, 3 wt% talc; (d) 3 wt% HFC-134a, 1 wt% talc; and (e) 3 wt% HFC-134a, 3 wt% talc.

Figure 4 displays the cell density plotted as a function of the degassing pressure as measured with the ultrasonic probes. Homogeneous nucleation (closed symbols, no talc) is indicated by a solid curve and reflects a solubility/concentration dependence, as reported in [13].

Figure 3. Cell density obtained under various conditions (talc content, HFC-134a concentration, temperature). Symbols are the same as those in Figure 1.

Figure 4. Cell density vs degassing pressure. Symbols are the same as those in Figure 1.

Heterogeneous nucleation (open symbols) can also be displayed through a master curve (dotted line), which intersects the homogeneous curve at a degassing pressure of 4 MPa, i.e., close to the critical pressure of HFC-134a (4.06 MPa). While the high nucleation density values obtained with 6 wt% HFC-134a could be explained by the classical theory, the results obtained with talc, surprisingly lying in the same cell density range, should be related to the number of particles, with expected maximum efficiency being one cell per particle, which is far from being achieved. Thus the presence of a nucleating agent modified the nucleation behavior for low degassing pressures, i.e., typically below the critical pressure of HFC-134a; above this 'threshold' pressure, presence of talc seems almost superfluous. Same comments can also be applied to results obtained by Park and coworkers on polypropylene foamed with CO₂ and isopentane [14]. While talc has enhanced the nucleation at a low concentration of CO₂, foams obtained with a higher CO₂ content (i.e. 3–5 wt%) that requires pressures above the critical pressure of CO₂ to prevent phase separation [15] yielded cell density numbers almost insensitive to the talc content. While PFA content and solubility conditions required that CO₂ and HFC-134a be processed in their supercritical state region, extrusion foaming with isopentane, well below its supercritical domain, always benefitted from the use of talc in the investigated conditions, as reported in [14].

Viscosity

Results of the shear stress as measured within the slit channel, for the different compositions in talc and HFC-134a content, are displayed in Figure 5. Based on the general behavior of filled polymer systems, one would have first expected a small but steady increase of the viscosity with the talc content [16]. It is thus surprising to observe jumps in the stress level as high as 6 kPa with the introduction of a small amount of talc particles. Moreover, reduction of viscosity is encountered in many cases, even with respect to the neat polymer.

The variation of the viscosity for filled polymer systems can be estimated using the equation:

$$\eta_r = \frac{\eta_s}{\eta_p} = \left(1 - \frac{\phi}{\phi_{\max}}\right)^{-2} \quad (4)$$

where, η_r is the relative viscosity, defined as the ratio of η_s , the filled polymer viscosity at the filler volume fraction ϕ , to η_p , the viscosity of the

Figure 5. Viscosity variations probed through shear stress under various conditions. Symbols are the same as those in Figure 1.

pure polymer; $\phi_{\max}$, the maximum packing fraction, accounts for the characteristics of the filler, namely the tendency of the particles to form agglomerates, their microstructure, and their resistance to breakup. For talc, a value of $\phi_{\max} = 0.44$ has been reported [16], which should be linked to its platelet-like geometry, and high aspect ratio. Using Equation (4), one can anticipate that the viscosity would not increase by more than 10% at 3 wt% talc.

Obviously, the results displayed in Figure 5 do not obey these expectations. For some conditions, viscosity reduction is even observed. These downward trends correspond roughly to a plateau in the degassing pressure results, as reported in Figure 1. Increase of the shear stress on the opposite is associated with increase of the degassing pressure. If heterogeneities in the PFA concentration could explain the higher degassing pressures, the same heterogeneities could also induce reduction of plasticization in the localized area due to PFA depletion that would explain the abnormally large stress increase with talc addition. Lack of heterogeneities with higher content of HFC-134a would therefore explain both stable degassing pressures and absence of strong fluctuations in the shear stress results.

Preliminary results on the viscosity variation for the PS-HCFC-142b-talc system have been previously reported [17]. As anticipated,

a viscosity increase was observed with the talc content varying from 1.3 to 14.3 wt%, although smaller amounts of talc yielded much higher viscosity augmentations than expected, possibly due to the antiplasticization effect related to the migration of PFA molecules as it will be proposed and detailed in the following section.

Proposal for Heterogeneous Nucleation Mechanism

In order to explain or validate the existence of a PFA-rich region at the polymer-particle interface, even the abnormally high concentration values speculated for the experiments conducted with 3 wt% HFC-134a, a mechanism based on the lowering of the surface energy through PFA molecules migration is proposed. The PFA concentration gradient will be possible through considerations that relate to the Gibbs free energy.

The phase structure that results for a multiphase system such as immiscible polymer blends is determined from its lowest free energy state, with respect to the chemical potential of the components as well as their interfacial tension, which will dictate to some extent the interfacial area and thus the geometry of the developed morphologies [18]. A good illustration for that relies on the work of Reignier and coworkers on the morphology of ternary polymer blends [18,19]. The morphology observed for the PMMA-PS-HDPE blends consisted of PMMA droplets encapsulated by PS shells and dispersed in a HDPE matrix. This structure enabled the minimization of the surface energy for this immiscible complex blend. The reported interfacial tensions were: PMMA-PS (2.4 mN/m) < PS-HDPE (5.1 mN/m) < PMMA/HDPE (8.6 mN/m). Moreover, these authors observed that a minimum PS shell thickness should be provided around the PMMA droplets to make this composite droplet behave as a pure PS droplet of constant size. Additionally, the shell thickness was proportional to the PMMA droplet radius and accounted for roughly 13% of the diameter of the composite droplet. PS was thus acting as a shield that dampened the surface energy of the PMMA with respect to the HDPE matrix.

Translating this to a gas-charged PS (miscible system) filled with a small content of mineral suggested that because of the large amount of surface generated by the talc, the PFA molecules should be dragged away from the neighborhood of the solid particle to minimize the difference in the surface energy between the nucleating agent surface and the PS matrix. Typical surface tension values for talc and polystyrene are, respectively, 41.6 and 42 mN/m [20], and that latter value for PS can be decreased to as low as 5–10 mN/m with the

presence of gas molecules. Reference [21] reports the variation of the interfacial tension of PS-CO₂ exposed to a CO₂-atmosphere as a function of the pressure. It is well known that pressure dictates the concentration of CO₂ that is dissolved in the PS matrix. Surface tension reduction is rapid for pressures below the critical pressure of the gas. Beyond that point, the reduction is moderate. A similar behavior was also observed for the low-density polyethylene with dissolved nitrogen [22]. Thus, within the low content region, a small concentration modification would impact the surface energy severely. Minimization of the interfacial surface energy between talc and polymer matrix would therefore necessitate the depletion of the plasticizing PFA molecules over a certain layer thickness surrounding the talc particle. This migration would therefore increase localized concentration of PFA, which was probed with ultrasound showing of higher degassing pressures than that associated with nominal values of PFA. At higher PFA concentrations that correspond to pressure close to or beyond the critical pressure of the gas, the lowering of the surface energy difference would necessitate too much segregation, which would not be 'cost efficient.' Why is the migration less relevant for 6 wt% HFC-134a but still effective for 10 wt% HCFC-142b, as reported in our previous study [10]? HCFC-142b is much more soluble in PS than HFC-134a; thus 10 wt% can easily be dissolved with pressures in the 3 MPa range, which is well below the critical pressure of HCFC-142b (4.15 MPa).

The strength of the polymer-filler interaction is related to the dispersive component (apolar, or Lifshitz-Van der Waals component) of its surface free energy, and not necessarily the apparent surface energy that also incorporates a polar or nondispersive, term [23]. We believe that the stronger the bond, the higher the amount of dragged gas molecules will be in order to balance the Gibbs free energy. For the same reason, fillers having low dispersive components will be prone to agglomerate, reducing the number of efficient particles suitable for nucleation. From these considerations, talc is a preferred choice in foam processing, as an efficient nucleating agent: high specific surface, strong interaction with polymer, with good dispersive potential.

Although it may sound unrealistic in the first place to have fluctuations of concentration for such systems, the segregation of the species in a miscible system can be clearly related to the lowering of the system's free energy. Maintaining certain regions of the system with a different composition than that of the bulk has obviously a free energy cost, which can be however minimized by avoiding steep concentration gradients [24].

If we associate the degassing pressures shown in Figure 1 with localized concentrations of HFC-134a induced by the presence of the talc particles, we may speculate that:

- For the trials conducted with only 3 wt% HFC-134a, the impact of the dissolved PFA molecules on the surface energy is large and yields migration of HFC molecules away from the talc surface in order to form areas of higher PFA concentration. These localized concentrated spots nucleate at higher pressures than the bulk. These spots do not interact for talc content of 1 and 2 wt%, and a plateau in the degassing pressures is observed. However, with 3 wt% talc, the density of particulates is such that intersection of concentrated spots yields areas with even higher PFA content, which are then associated with higher degassing pressures. This is schematically illustrated in Figure 6.

Figure 6. Schematic model for the PFA gradient in the polymer matrix near the talc particles.

- At higher HFC-134a content, i.e., 6 wt%, degassing occurs at a pressure close to that of the critical pressure, P_c , of the PFA. Variation of the concentration in that region has less impact on the surface energy, and migration is then less favorable, but still significant, as it can be observed from the slight increase of the degassing pressures with 1 wt% talc.

CONCLUSIONS

A qualitative model, based on degassing conditions probed by ultrasound, has been proposed for nucleation induced by nucleating particles. In the presence of talc, higher degassing pressures have been observed that were associated with hypothetical high PFA content patches localized near solid particles. Concentration gradients of HFC-134a were assumed considering free energy concepts. Depletion in PFA at the vicinity of talc particles was also justified through rheological measurements, although this ternary mixture (polymer-PFA-filler) remains rheologically complex. At relatively high concentrations of HFC-134a, heterogeneous nucleation did not impart significant improvement on the cell density, and this behavior was linked to near-critical conditions for the HFC at this PFA concentration.

Obviously, surface energy of the nucleating particle, as well as its geometry, should be taken into account in the heterogeneous nucleation process. The interaction of the particles with the polymer macromolecules should be considered in terms of work of adhesion, with possible impact of the structure of the polymer chain (molecular weight and long chain branching), as observed through degassing pressures again in another study [25]. The heterogeneous nucleation is a complex process, and more work is needed to fully understand it.

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