PARTICLE NUCLEATION IN CHEMICAL FOAM EXTRUSION

Peter Schroeck and Randy Minton
Reedy International Corporation, Charlotte, North Carolina USA
Tel: 980-819-6930, email pschroeck@reedyintl.com

BIOGRAPHICAL NOTE

Peter joined Reedy International in 2004 as a Sales Account Manager. He was named Technical Sales Director in 2007. Overseeing the company’s growth in Asia, Mexico, Canada and South America, he was named Chief Business Development Officer in 2010. In 2013 Peter was named President of Reedy International upon the passing of Michael Reedy.

ABSTRACT

Recent emphasis on light-weighting has foaming technologies being explored by all facets of industry. Endothermic chemical foaming agents are especially desirable due to low-to-zero impact on the environment. Different methods of nucleation to control the cells formation are offered to control cell growth and ultimately part performance.

INTRODUCTION

Foaming agents for thermoplastics have been utilized for decades. All typical conversion processes are candidates for foam. In extrusion, physical blowing agents can be used depending on low density and cost targets while chemical foaming agents (CFA) have often been used as the sole gassing agent in high and medium density foams, or in tandem with physical foams to achieve particular cell qualities. In either case, it is necessary to introduce gas that can be completely dissolved in the polymer melt and kept under appropriate pressure until released from the die.

Adequate system pressure and a well-designed extrusion die will ultimately be the greatest predictors of foam success, however physical nucleators like talc are often used to create more “hot spots” where a cell can form. Closed-cell structure is crucial in keeping mechanical properties and part characteristics.

Polyethylene, polystyrene and PVC extrusions have been foamed very convincingly for some time. Foam polypropylene (PP) has been a relatively recent focus of many markets from food trays and films, to cable jackets and filler rods, to automotive interiors and body-side moldings and sub-sea gas pipe owing to different process and performance benefits. Filler rods for example, need to maintain a particular dimensionality and meet set compression standards, while sub-sea pipe requires superior thermal insulation, low temperature crack resistance and ability to withstand high burst pressure.

CHEMICAL FOAMING AGENTS

Chemical foaming agents are those that decompose under influence of heat. The CFA must reach its full activation far enough below the processing temperature to ensure that all the gas is expanded, but not so far below that the cells form too early, potentially causing the closed cells to expand too large, where they may coalesce to become “voids” rather than proper individual cells. Alternately, they may become oddly shaped or completely collapse, negating the foam benefit.
Azodicarbonamide (ADC) has held the largest share of the chemical foam market since its inception. An exothermic, or heat-generating CFA, it releases N₂ gas into the polymer matrix and can impart high-pressure, rapid expansion at approximately 210°C resulting in significant weight savings. However toxic byproducts have already resulted in ADC’s disqualification from certain food packaging industries in the EU and in children’s products manufactured in China, such as toys and soft mats. It has recently been placed on SVHC (Substances of Very High Concern) watch pending further data. This fact has shifted most developmental programs to endothermic CFAs, such as Reedy’s SAFOAM or Clariant’s Hydrocerol line.

Endothermic CFAs are generally created by sodium bicarbonate, citric acid salts and combinations thereof. A more gradual expansion, endothermic CFAs may begin decomposition as low as 125°C and as high as 200°C. Residual solids create nucleation that results in very fine cell structure and superior solubility in the melt. The CO₂ created is a low pressure gas that will act as a plasticizer, allowing a reduction in melt temperature, part of a series of benefits that will lead to a faster cycle time.

Particle size of the CFA itself can contribute to final cell size in the core. However particle size of the CFA is not the prime factor in an optimized process. The pressure at which each respective gas is soluble in the polymer melt plays a bigger role. N₂ needs to remain at pressures near 3000 psi while CO₂ needs only 1450 psi. If the ADC foam process does not remain at this pressure, pre-foaming and cell coalescence can occur which can negate the advantages of small particle size. The particle size of the foaming agent alone will be responsible for cell size. System pressures above 1450 psi are common, allowing process and die-exit pressure to be the prime factors in cell size using CO₂. For this reason, an endothermic CFA with a particle size of 25 or even 50 micron can conceivably lead to smaller cells than an exothermic CFA with a 3 micron particle size with inadequate back pressure.

Reedy international has always touted the benefits of food- and medical-safe endothermic CFAs like SAFOAM, with zero ODP (ozone depletion potential) or GWP (global warming potential). The resulting tests concentrate on utilizing these products. We will focus on endothermic (heat-absorbing) chemical foaming agents and particle nucleators chosen from Reedy’s SAFOAM line.

POLYPROPYLENE FOAM EXTRUSION

Worldwide revenues generated by polypropylene are expected to grow considerably due to its versatility of applications. An annual growth rate of 4.4% in the first decade of the 2000s is expected to be surpassed in the current decade, reaching US$145 billion by 2019. Flexible and rigid packaging are the major consumers. Good candidates for foaming agent additives should have a good balance between stiffness and impact strength², and the polymer should have adequate melt strength to “trap” a well dispersed cell structure in place. High Melt Strength PP like the Daploy line by Borealis are designed specifically for foam extrusion, focusing on thermoformability and allowing PP foam densities from 40 to 700 g/l³ depending on process. Other major PP companies are in various stages of development on competing technologies.

FOAMING AND NUCLEATION EXAMPLES

Reedy has recently acquired a sheet foam line which is currently undergoing commissioning. As part of the initial start-up, foamed samples of a 2.8 MFI extrusion grade polypropylene homopolymer (Exxon PP4712E1) were processed in combination with two different Reedy CFA’s and nucleator masterbatches. A proprietary experimental nucleator formulation was also evaluated and compared.

It was observed during the start-up of the sheet line that the extruder output was too low to maintain adequate back-pressure to keep the CO₂ gas generated in solution. Consequently the samples produced did not have an optimized foam structure. In spite of this the samples obtained did illustrate the contribution of physical nucleators to cell size and density.
TABLE 1: Sheet Foaming, CFA and Nucleation Series

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>CELL DIMENSIONS (μ)</th>
<th>CELL VOLUME (cc)</th>
<th>DENSITY (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4712 1% PN-40E</td>
<td>250 x 50</td>
<td>0.785 x 10^-5</td>
<td>0.800</td>
</tr>
<tr>
<td>4712 1% PE-50</td>
<td>250 x 45</td>
<td>0.636 x 10^-5</td>
<td>0.789</td>
</tr>
<tr>
<td>4712 1% PE-50+3% X14-001A</td>
<td>220 x 35</td>
<td>0.338 x 10^-5</td>
<td>0.739</td>
</tr>
<tr>
<td>4712 1% PN-40E+1% PSN-510</td>
<td>225 x 40</td>
<td>0.452 x 10^-5</td>
<td>0.789</td>
</tr>
<tr>
<td>4712 1% PE-50 1% PSN-510</td>
<td>240 x 40</td>
<td>0.482 x 10^-5</td>
<td>0.711</td>
</tr>
<tr>
<td>4712 1% PN-40E+1% CAN-550</td>
<td>230 x 40</td>
<td>0.462 x 10^-5</td>
<td>0.804</td>
</tr>
</tbody>
</table>

**Chart of Cell Size and Foam Density**

It can be seen from the table and chart that cell size, even in an un-optimized foaming process, can be dramatically lowered through the use of physical nucleators. Density remained moderately constant with respect to the amount of CFA used while the dimension and number of cells decreased and increased respectively.
1% PN-40E

1% PE-50
The above photos show all the nucleated samples. Proprietary experimental nucleator X14-001A illustrates smaller, more numerous and most uniform bubbles.

COMMERCIAL TRIAL

In a recent commercial foam extrusion trial of polypropylene cable filler rod, a prospective client sought an improved density reduction, while maintaining specifications regarding shape (2.51mm) and crush strength (not defined).

Incumbent CFA allows approximately 8% density reduction while maintaining physicals and ovality. Goal for this trial was to achieve 15% density reduction while maintaining physicals and ovality.
You will see in the table above (TABLE 2) that foaming ranged between a low of 7.6% and as much as 42% density reduction. Trials that saw the greatest density reductions, (#3, #4) were difficult to control and ovality was lost. However tests #2 and #5 proved commercially viable at an improved density reduction for the customer of 19.5% with a let down ratio of 2 parts CFA to 1 part particle nucleant allowing more than twice the density reduction with ovality and crush strength within specifications. The pictures below indicate a well-controlled, closed-cell structure with little variation.
Polypropylene Filler Rod, 2% PN-40E, 0.721 g/cc Density

Polypropylene Filler Rod, 2% PN-40E + 1% PT-40, 0.727 g/cc Density
CONCLUSIONS

Developments in thermoplastic foam extrusion will allow established markets greater reduction of costs. Resins formulated to maximize foam performance will allow plastics like polypropylene to move more adeptly into applications previously reserved for engineering resins. Performance and process enhancing cellular nucleating additives will give converters flexibility to meet each unique criteria.

REFERENCES

1. Market Study: Polypropylene - 2nd edition (UC-4205)
2. ExxonMobil Products & Services brochure (2014)
3. Borealis technical sheet, Daploy WB130HMS

ACKNOWLEDGEMENTS:

The authors would like to thank ExxonMobil, Braskem and Genpak for supplying samples and technical service.