

Low-Density PET Foam, Part 1

Introduction

The class of thermoplastic polyesters has two major subclasses - polybutylene terephthalate or PBT, and polyethylene terephthalate or PET - and two minor subclasses - PET copolymer such as Eastman's PETG, and polyethylene naphthanate or PEN. With the exception of the copolymers, all polyesters can be crystallized, albeit very slowly when compared with polyethylenes. Of the majors, PBT resin is more expensive to produce than PET and so has found use as a highly filled or reinforced engineering resin that can be foamed to about 70% of the unfoamed resin density. Virgin PET is currently selling for less than \$0.50/pound and finds extensive use as amorphous sheet in packaging and as biaxially oriented crystalline shapes in barrier containers. Crystalline PET has a glass transition temperature of about 70°C and a melting temperature of about 265°C. All thermoplastic polyesters are "condensation polymers", meaning that the polymer molecular weight is increased by eliminating a small molecule such as water. Like most condensation polymerizations, the PET polymerization is reversible. PET molecular weight is usually determined by wet chemistry solution viscosity, and is usually reported as inherent viscosity, $[\eta]$, or intrinsic viscosity or IV. One relationship between $[\eta]$ and number-average molecular weight is:

$$[\eta] = 7.50 * 10^{-4} (M_{\eta})^{0.68}$$

The standard relationship between shear viscosity and number-average molecular weight is:

$$\eta_s = \alpha (M_{\eta})^a$$

where α is dependent on the type of polyester and a is on the order of 3.4. The fiber grade PET has an IV range of about 0.6 to 0.7. Bottle grade PET has an IV range of 0.7 to perhaps 0.9. Special techniques are needed to achieve IVs in excess of about 0.9. The most common technique is solid state polymerization. Traditional solid stating operations require hours of elevated temperature and relatively high levels of vacuum to achieve IVs in the 1.2 to 1.5 range.

One of the earliest uses of the crystalline form of PET was in the ubiquitous thermoformed ovenable "TV dinner tray", first commercialized in the mid-1980s. The technique for producing this product is quite unique. A PET of about 1.0 that has been doped with nucleants and impact modifiers is extruded as a sheet and quenched to minimize crystallization. The sheet, with no more than 5% crystalline, is then heated very rapidly to the forming temperature of around 150°C to 160°C. Since PET is a very slowly crystallizing polymer, only a small amount of crystallization, up to about 10% or so, has taken place before the sheet is stretched under pressure against a mold heated to 170°C to 180°C. The PET crystallizes against the hot mold to about 20 to 25%. This level of crystallinity is sufficient to rigidify the shape against 200°C hot air oven use for one hour

Low-Density PET Foam, Part 2

Summary of Part I

In [part I](#), I discussed the general types of thermoplastic polyesters, noting that polyethylene terephthalate or PET is a slowly crystallizing polymer that has a melting temperature of about 260 °C. It is considered a likely candidate for many high-temperature applications, particularly since it is relatively inexpensive when compared with other high-temperature polymers such as polyamides. Foamed crystalline PET is considered a candidate for higher temperature thermal insulation applications. Part II of this Technical Minute focuses on the desired properties of foamed PET.

Packaging Applications

Crystalline polyethylene terephthalate is called CPET in the written literature. When the polymer crystallinity is in the 20% range, the polymer is tough at room temperature. At temperatures greater than the glass transition temperature of about 70 °C, it is pliable but retains its shape until temperatures in excess of about 200 °C. CPET at 40% crystallization level is quite brittle. Unfoamed CPET has been thermoformed into "TV dinner trays" for more than a decade, where the tray is exposed to "recommended" convection oven temperatures of 175 °C to 180 °C for up to 60 minutes without deterioration. However, the traditional unfoamed tray suffers from several limitations:

- It is difficult to keep PET from crystallizing during extrusion when the sheet thickness is in excess of 0.060 inches or 1.5 mm. As a result, thermoforming is restricted to relatively shallow shapes. This obviates certain applications, such as bakery containers, which require relatively deep containers.
- In addition to the restriction on the depth of draw, container stiffness becomes a problem when the side walls of the container becomes too thin. Keep in mind that flexural stiffness, S , is given as:

$$S = EI$$

where E is the modulus of the polymer and I is the moment of inertia. For a thin beam, b in width and t in thickness, the moment of inertia is given as:

$$I = bt^3/12$$

It is apparent that stiffness is proportional to the container wall thickness to the cube power. For economy, it is desired to keep the wall thickness as thin as possible. Therefore the container wall can become quite flexible, particularly above T_g , where the PET modulus drops dramatically.

- When unfoamed PET is thermoformed, two types of crystallization occur. The first, thermal crystallization, dominates, effectively locking the shape into its final configuration until the product temperature is raised to the PET melting temperature of about 260 °C. However the PET sheet is also biaxially stretched, and a second type of crystallization, orientation crystallization also occurs. Certainly, the level of orientation increases as the draw depth increases. This added crystallization level may make the CPET product more brittle than

tough.

- And, in a typical food container application, the product placed in the CPET container is flash frozen at temperatures of about -30 °C. PET at this temperature is 100 °C below its glass transition temperature. It is brittle, much like PS is at room temperature. As a result, special care must be taken to minimize "rough handling" such as impact during filling, flash-freezing, and shipping of frozen product. Otherwise, the product may be compromised by broken corners and split sealing regions.

Impact and Foaming

Even though it is well-documented that biaxial orientation of a brittle polymer increases its toughness, it is also well-known that the impact strength of a brittle polymer does not necessarily increase by foaming. However, foaming does alter the nature of flexural impact failure. Foamed CPET fails by crushing under impact, instead of failing catastrophically, as unfoamed CPET does. That is, individual CPET membranes bend, then break under impact, with impact energy being dissipated first to the intersections of the membranes, then to neighboring cell membranes. As a result, even though many membranes rupture under impact, the foam structure remains essentially intact, thereby protecting the product. This effect is well-known for polystyrene foam, where the container of low-density polystyrene foam is used to protect refrigerated eggs, for example.

However, one must be careful to recognize that the transition from catastrophic failure to non-catastrophic, crushing damage occurs at relatively high foaming levels. For example, polymeric structural foam, where density reduction usually does not exceed 50%, fails under impact in much the same way as the unfoamed polymer. Density reduction of more than 50% and usually 90% is needed in order to achieve crushing rather than catastrophic failure.

Stiffness and Foaming

As noted above, container stiffness is proportional to the container wall thickness to the cube power and to the modulus of the polymer to the first power. At the same container weight, foaming increases the effective wall thickness of the container. But foaming decreases the effective modulus of the container. It is well-known that the modulus of a foamed polymer decreases in proportion to the square of the foam density:

$$E_f = E_0 (\phi_f / \phi_0)^2$$

At the same container weight, the sidewall thickness increases in inverse proportion to the foam density:

$$t_f = t_0 (\phi_f / \phi_0)^{-1}$$

Therefore, we can easily show that at the same container weight, the container stiffness increases with decreasing foam density:

$$S = E_f I_f = E_0 I_0 (\phi_f / \phi_0)^{-1}$$

In short, by foaming, we can improve two critical aspects of container performance - impact strength, particularly at freezer temperature, and sidewall stiffness, particularly for deep-draw containers.

The real question that remains is: Can we produce a CPET foam having up to 90% density reduction?

The Practical Aspects of Foam Density Reduction

The foam industry has long believed that certain polymers foam to what has been called "natural densities". For example, polystyrene and HDPE seem to foam well at a natural density of about $2.2 \text{ lb/ft}^3 = 35 \text{ kg/m}^3$, whereas PP seems to foam well at about 10 to 15 kg/m^3 . PVC, on the other hand, is difficult to foam to densities less than about 100 kg/m^3 . And, it is thought, PET should also be difficult to foam to densities less than about 100 kg/m^3 .

The natural density belief has some basis in fact. The production of low-density foams involves, as the terminal phase of the process, the biaxial stretching of membranes. As discussed in detail elsewhere [JLThrone, [Thermoplastic Foams](#), Sherwood Publishers, 1996 - see this Web page for ordering information], the available stretching force is directly related to the differential pressure between the cell gas and the environment of the forming foam. The resistance to the stretching force is viscoelastic character of the polymer film, which is experiencing strain hardening and rapid cooling. If the stretching force is too high or the resistance to the stretching force is too low, the film may rupture, which may result in catastrophic foam collapse. If the stretching force is too low or the resistance is too high, the film may not stretch sufficiently, and the foam density may not achieve a desired low value.

Many polymers can be uniaxially stretched to 4X or more near but above their transition temperatures, before rupturing. This implies that foams of 30X density reduction are achievable before catastrophic collapse. For PS, for example, this predicts a foam density of 35 kg/m^3 . This further implies that for CPET, and PVC for that matter, foam densities of 45 kg/m^3 are achievable, given the correct processing conditions. The key phase here, of course, is "correct processing conditions". [Some processing conditions were discussed in [Part I](#), but additional discussion will be found in an upcoming Technical Minute.]

So, to summarize this part, foaming of CPET to low densities for commercial container applications is justified by improved performance at low temperatures and improved stiffness for deeply formed containers.

What about thermal insulation? Does CPET have adequate insulating properties? Part III addresses this question.

[Jim Throne](#)

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or more. Currently, approximately 100 million pounds of CPET or "Crystallized PET" are consumed in the US each year, with a projected growth of about 5% APR.

Until earlier this year, the historically high cost per unit volume of PET, when compared with PS, restricted the market development as a PS replacement in other packaging areas, including foams. This was also valid for products such as generic insulation board and pipe insulation, this despite the much higher continuous use temperature capability of PET. The current worldwide excess capacity of PET has driven virgin bottle- and fiber-grade prices to record lows. While higher IV grades have not seen price reductions as dramatic, certain higher performance styrenic foam applications are now economically feasible targets for PET foam. Three general markets have been targeted:

- ✍ Transportation, for head liners, automotive insulation pads and coolant fluid hose insulation covers. The typical density range is 100 to 300 kg/m³. The polymeric competition is SMA. The annual US market is estimated to be about 10,000 tons.
- ✍ Packaging, for niche applications between compact CPET and olefin and styrenic foams. The typical density range is 350 to 700 kg/m³. The product requires high-temperature FDA approval. The market size is estimated to be about 25,000 tons.
- ✍ Construction, for high-temperature metal surface insulation applications. The anticipated density range is 30 to 100 kg/m³. The competition is glass fiber and mineral wool. The market size is estimated to be about 20,000 tons.

The Development of a PET Foam

It is well-known that a melt viscosity is a primary material property in the formation of stable bubbles. Early attempts to foam bottle- and fiber-grade PET were unsuccessful, since no processing window could be found. The polymer could not be cooled sufficiently to prevent bubble collapse before it crystallized. PET copolymers and PETs with IVs in excess of 1.0 could be foamed but were too expensive. These limitations have been relaxed recently, with less expensive copolymers and more rapid molecular weight appreciation techniques. Thin PET foam sheets (less than 0.100 inch) with nominal densities of 100 kg/m³ have been commercially made, and foams with densities of 60 kg/m³ have been made experimentally. Crystallinity levels of 15% or so have been achieved, although very thin sheet tends to have much lower crystallinity. Thick PET foam plank (1 inch or so) has been continuously extruded at densities of 80 kg/m³ and crystallinity levels of 25% or so.

PET foams has been successfully produced on the three major types of foam equipment - twin-screw, two-stage single screw and tandem. PET has been foamed with hydrocarbons, HCFCs, carbon dioxide, and combinations thereof. Classically, a chemical nucleating agent/foaming agent such as AZNP, 5PT and / or an endothermic foaming agent, is added at 0.1% to 0.2% (wt). Care must be taken using talc as a bubble nucleator since it also acts as a crystallite nucleator. An excess of talc will yield a brittle foam. In fact, care must be taken with all adducts to ensure that the adduct does not carry adsorbed water into the extruder or produce water as part of its decomposition reaction. As a result, it is recommended that PET be dried at 160°C for at least 4 hr prior to extrusion. All reclaimed regrind must be dried to the same intensity. A small quantity of water, typically less than 50 parts per million, will cause substantial deterioration in PET IV. [Chemical blowing agents

such as NaHCO_3 or any of the modified bicarbonates produce water as a decomposition product and so must not be used. AZNP and 5PT can also be problems since they produce by-products such as ammonia, which will degrade PET.]

The standard PET plasticating extruder temperature profile is 200(°C)-280-270- through the melt pumping stage. Melt pressure at the physical foaming agent inlet should be in excess of 100 atm. Although sophisticated plasticating screw sections are commonly used in PS and PE foams, they should be avoided in PET foaming, since excessive shear leads to thermal degradation. The same is true for excessive dissipative mixing downstream of the blowing agent inlet. PET seems to run satisfactory on a standard PS screw, and in fact plasticizes like PS, albeit at melt temperatures that are about 100°C higher.

As with all foamable melts, cooling is critical. The gas-laden PET melt should be delivered to the extrusion die at about 185°C or about 85°C or more below the traditional PET melt temperature and about 10°C below its recrystallization temperature. As with all foamable melts, the melt pressure at the die entrance should be 100 atm or so. For PET, a higher melt pressure is needed to prevent premature foaming inside the die, an effect that leads to poor final product surface quality and fibrillation at the die exit.

Twin-screw extruders, two-stage or long single-screw extruders, tandem single-screw extruders and twin-screw-to-single-screw tandem extruders have all been used to produce production quality foams. The key to effective tandem foam extrusion seems to lie in quality gas seal at the secondary extruder screw bearing. Reverse flighted melt seals are only partially effective in achieving quality gas seal. Since the blowing agent dosage for PET is usually quite low [on the order of 3% (wt) or so], any gas loss through any aperture in the barrel will dramatically affect the foam quality.

Since PET foams at much higher gas-laden melt temperatures than either PE or PS, higher boiling point blowing agents are needed. HCFCs that have been used successfully include 134a, 142a and 152a. Their properties are given in [Thermoplastic Foams](#) [follow this link to see information elsewhere on this web page about ordering this book]. Although isopentane or i-C5 produces an adequate foam, hexane produces a much more uniform foam with the classic halo around the foam die. Since there are environmental concerns about using C6, a combination of heptane and isopentane seem to produce a foam quality similar to that foamed with C6. Carbon dioxide, by itself, does not produce a useful foam. Although the cell size of a PET foamed with CO₂ is extremely fine, the corrugations normally produced with a very low boiling foaming agent are so severe as to render the product useless. [The causes and mitigation for corrugation is given in another Technical Minute.]

[Jim Throne](#), 25 June 1997

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