

Recrystallization – What Does That Mean?¹

In the last TF101, I mentioned recrystallization. In this tutorial, I will explain what it is and why it is important in thermoforming.

Amorphous and Crystalline Plastics - A Brief Review

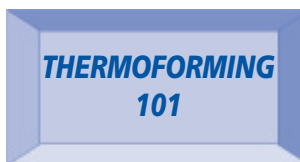
In a very early lesson, we learned that there are two general classes of plastics used in thermoforming. Plastics such as polystyrene, ABS, polycarbonate and even rigid PVC are considered amorphous. That is, they are glassy-brittle at room temperature. When they are heated to a general temperature range called the glass transition temperature, they become rubbery. If we continue to heat them, they become less and less rubbery and more and more fluid-like. When we cool these polymers to their glass transition temperature, they immediately become glassy-brittle again. Amorphous polymers represent the majority of plastics thermoformed today.

But as we learned in that early lesson, thermoformers are bent on forming crystalline - or more correctly, semicrystalline - polymers such as polyethylene, polypropylene and PET. For many years, polyethylene was the only semi-crystalline plastic that was widely thermoformed. PET is usually formed in the amorphous state (as APET). Special processes are needed to produce crystalline PET structures.

Melt Forming PE

High-density PE has exceptional hot melt strength above its melt temperature of about 275°F (135°C). That's

why the blow molder can extrude a tube of polyethylene, then capture it in a clamshell mold to make a bottle. Thermoformers also rely on the hot melt strength of it in sheet form. We heat the sheet above its melt temperature just prior to forming it, as a melt. Polyethylenes are 50-80% crystalline and the sleek shape of the molecule allows very rapid crystallinity once the formed part is cooled below its melt temperature. As a result, HDPE is



the most successful semicrystalline polymer thermoformed.

Solid State Forming of PP

Until recently, polypropylene recipes did not have sufficient hot strength to remain sheets in the thermoforming ovens. As a result, PP was thermoformed in the *solid state*. What this means is the PP sheet was (and is) heated to just below its melting temperature range, which is about 330°F (165°C) for homopolymer polypropylene (homoPP). PP becomes rubbery in a very narrow temperature range just below the melting temperature.

There are two reasons for this rubberiness. First, the crystallinity of PP is about 50%, meaning that about half the PP is not locked in crystallites, but is instead in an amorphous state. The glass transition temperature of homoPP is about 15°F (-10°C). So when homoPP sheet is at a forming temperature of about 320°F (160°C), say, the amorphous portion of the sheet is 305°F (170°C) above its T_g². Secondly, imperfect crystallites tend to melt below the stated melt temperature. This means that more polymer is added to the amorphous side of the equation, making the sheet even more rubbery.

With sufficient pressure then, we can squeeze, push and otherwise press PP

against the mold. Pressures of 50 to 100 psi have been used to do just this.

So, what is the problem with solid state forming of PP? Really, nothing. It just requires higher forming pressures than what would be used for, say, PS. Oh, and the product is not water white but instead, about as translucent as the original sheet. This is because we don't melt out the crystallites and the crystallites are of sufficient size to interfere with visible light (0.4 to 0.7 microns).

Melt Forming of PP

Copolymerization of polyethylene in PP and now, short- and long-chain branching of PP has greatly improved PP hot strength. This lets us to thermoform PP in the melt state, or the state where all the crystallites are fully melted. Copolymer PP or coPP usually melts around 310-320°F (155-160°C).

But melt forming PP is not like melt forming polyethylene. We run into a very difficult problem. PP recrystallizes at a much slower rate than polyethylene. Even when coPP is cooling at 9°F/minute (5°C/minute)³, it recrystallizes around 210°F (100°C), or about 100°F (60°C) below its melt temperature. Small amounts of recrystallization rate enhancers such as sorbitols can increase the recrystallization temperature by about 20°F (10°C). While this may shorten the hold time on the mold, we still need to hold coPP on the mold longer than we might think.

And more importantly, we need to be concerned about recrystallization that might continue long after we remove the formed coPP part from the mold surface. When the formed part isn't constrained, different areas of the part can crystallize at different rates and to different crystallinity levels. Distortion, warping, cupping, and general mayhem can occur long after the part is formed. ■

Keywords: *Recrystallization, solid state forming, melt forming, hot melt strength*

¹ **Thermoforming 101** is designed to be a tutorial on the basic building blocks of the thermoforming industry. The first series of lessons concluded in TFQ 21:3, 2002. This is another in the second series of lessons that have as their objective to fill in the gaps from the first series of lessons.

² Compare this with PS at its thermoforming temperature of 350°F (175°C), or 140°F (75°C) above its T_g of 210°F (100°C).

³ In practice, we would never cool PP this slowly. The test equipment used to measure melting and recrystallizing temperatures operates at about this cooling rate.