

Amorphous and Semi-Crystalline Plastics

The structure of molecular chains on the nanoscale and microscale has profound effects on the properties of a polymer. This article will focus on the differences between amorphous and semi-crystalline thermoplastics. Thermoplastics are polymers which soften and flow above a certain temperature, where they can be formed into some new shape, then cooled. The heat, reform, cool cycle can be repeated, in contrast to thermoset polymers, which cure and rigidly maintain their shape after the first cycle due to a permanent chemical crosslinking process.

Microstructure

Polymer chains are made up of repeating chemical units, called monomers, which are polymerized, or linked together, through different chemical processes. Most common industrial thermoplastics have a carbon backbone, meaning that carbon-carbon bonds run the length of the polymer chain. The carbon-carbon bond has a length of about 150 pm, or about a million times smaller than the diameter of a human hair. A polymer chain is made of tens of thousands to hundreds of thousands or even millions of repeating units.

In amorphous thermoplastics, the individual polymer chains in a given volume are unordered, snaking around each other and forming entanglements, much like a bowl of spaghetti or a head of long, uncombed hair. On the other hand, semi-crystalline plastics form regular, repeating structures, or crystalline regions, which are linked together by amorphous regions.

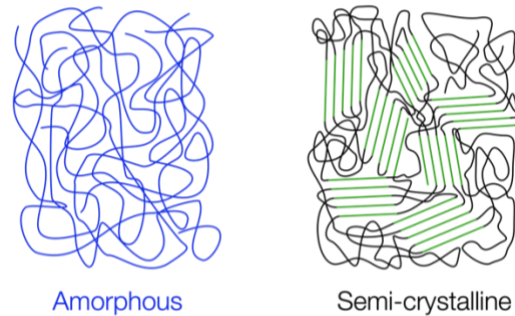


Figure 1. Amorphous and semi-crystalline polymer structures

Molecules line up into regular units called lamellae, with oscillations on the order of 20-60 nm. Those lamellae can form several kind of structures, but they most commonly form into spheroid structures called spherulites, which can have a size between 1 and 500 μm , as depicted in Figure 2. For comparison, the average human hair is often considered to be about 80 μm , although it can range from about 20 to 180 μm . The human eye can resolve lines around 12 μm in diameter, so if a sample is prepared properly, one could actually see spherulites with the naked eye! Prepared on a hot stage microscope with cross-polarized light, spherulites make for beautiful images, seen in Figure 3.

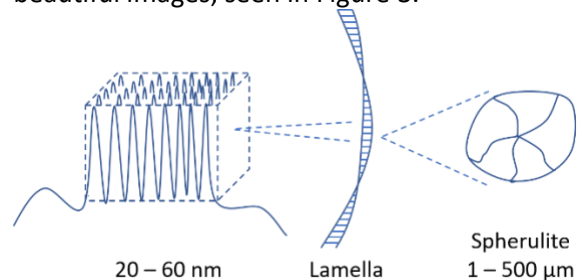


Figure 2. Crystalline regions form into lamellae, which form around a nucleation point into spherulites.

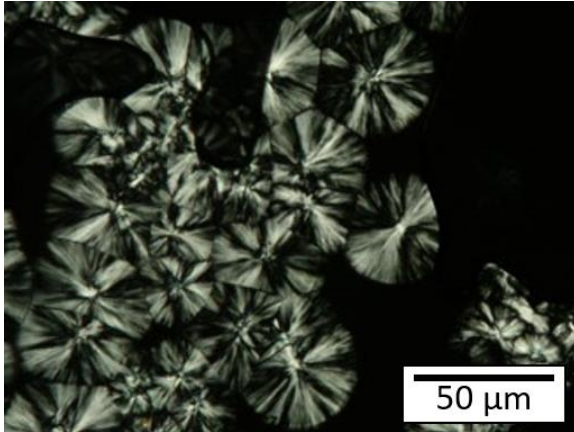


Figure 3. Spherulites seen in a blend of polypropylene and polyethylene. Courtesy of Dr. Chuanchom Aumnate, Chulalongkorn University, Thailand.

In fact, it is these crystalline structures that lend themselves to the most visible difference between amorphous and semi-crystalline plastics. Many amorphous plastics are optically transparent, such as polystyrene (PS) and polycarbonate (PC); others like polyetherimide (PEI) are transparent but have a yellowish hue. On the other hand, semi-crystalline plastics tend to be translucent or opaque, depending on the thickness of the part (see Figure 4). That's because the spherulites are larger than the wavelength of visible light, which is from 380 to 700 nm. The semicrystalline regions have a different index of refraction than the amorphous regions and so light is scattered as it passes through the material. The result is a milky or translucent plastic, such as polyethylene or polypropylene.



Figure 4. Optical clarity of an amorphous sheet of plastic vs. a semi-crystalline sheet.

The rule isn't always true, though. Polyethylene terephthalate (PET), the material for plastic bottles, is a semi-crystalline material, but the bottles are frozen in molds faster than crystals can grow large enough to scatter light, leaving them clear. Polyvinylchloride (PVC) can be clear, but it is often colored or filled with minerals, as with PVC pipe.

Structure-Property Relationships

There are a wide range of properties available across the polymer pyramid, shown below in Figure 5. Moving up the pyramid from commodity to ultra-performance polymers generally correlates to increases in strength, stiffness, chemical resistance, wear resistance, temperature performance, and of course cost. For materials in the same performance tier, amorphous polymers tend to be more tough and ductile, while semi-crystalline polymers can be stronger, more wear resistant, and more chemical resistant. We will take a look at how different properties vary based on the microstructure.

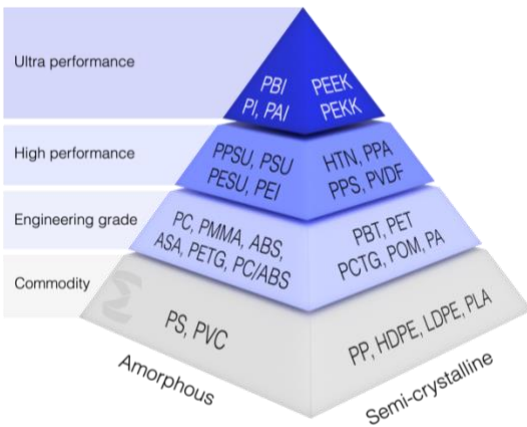


Figure 5. Polymer pyramid divided by amorphous and semi-crystalline thermoplastics.

Thermal Properties

Amorphous and semi-crystalline plastics can be differentiated by their characteristic temperatures. Amorphous plastics have a glass transition temperature (T_g), below which they are hard and glassy, like polystyrene (PS) at room temperature, and above which they become molten and formable. Above T_g , the molecules have enough free volume between them to slide past each other readily.

Semi-crystalline polymers also have a T_g , but above that point they are rubbery and strong, not glassy. That's because, although the amorphous regions are now more mobile, the crystalline regions are still dense and ordered, contributing to the stiffness of the material. This effect is more pronounced for semicrystalline polymers with a higher degree of crystallinity. For example, polyethylene (PE) is above T_g at room temperature (think milk jugs, kayaks, and plastic bags). Polypropylene (PP) is also above T_g at room temperature, but its T_g is around $-10\text{ }^\circ\text{C}$ ($14\text{ }^\circ\text{F}$), so it will become brittle in a cold freezer or in a garage in the winter, which can lead to broken toys, garden tools, or storage containers

(some of the common uses for PP). Semi-crystalline polymers also have a characteristic melting temperature (T_m) at which the crystalline regions melt and become amorphous. It is at this point that they lose rigidity and become a polymer melt. Table 1 shows the T_g and T_m for several common polymers.

Table 1. Characteristic temperatures for some common plastics. Adapted from Baur, Osswald, and Rudolph, *Plastics Handbook*, Hanser, 2019, and *Matweb, www.matweb.com.

	Abbr.	T_g [$^\circ\text{C}$]	T_m [$^\circ\text{C}$]
High Density Polyethylene	HDPE	- 110*	110
Polypropylene	PP	-10	165
Polystyrene	PS	97	-
Polycarbonate	PC	150	-
Acrylonitrile Butadiene Styrene	ABS	95	-
Polyethylene Terephthalate Glycol	PETG	81*	-
Poly Cyclohexylenedimethylene Terephthalate Glycol	PCTG	81*	213
Polyphenylsulfone	PPSU	219*	-
Polyetherimide	PEI	215	-
Polyether Ether Ketone	PEEK	145	340
Polyether Ketone Ketone	PEKK	165	391

One difference between amorphous and semi-crystalline polymers, which is important especially in the context of additive manufacturing, is the behavior during cooling. Amorphous polymers have a continuous but non-linear change in their specific volume at the T_g , and because of this the shrinkage upon cooling is fairly easy to account for. The primary strategy to reduce shrinkage and warping in amorphous polymers is to increase the chamber

temperature of the printer close to the glass transition temperature of the polymer.

Semi-crystalline polymers experience a large change in density over a relatively small temperature range around the peak crystallization temperature due to the formation of the crystalline regions. Therefore, semi-crystalline polymers typically experience greater overall shrinkage compared to amorphous polymers. Some semicrystalline polymers such as PLA can be printed with less warping by quickly cooling them below their peak crystallization temperature to quench them into a low crystallinity state. Because almost all AM processes deposit material layer by layer, this larger shrinkage, applied at every layer, leads to a higher tendency for the part to warp. This tendency can be reduced with the addition of fiber fillers into the plastic, which both increase the material stiffness and reduce the thermal shrinkage.

It's worth noting that some semi-crystalline polymers, such as PCTG and PEKK, tend to crystallize slowly. Essentium's clear PCTG can be used to print transparent parts. If higher crystallinity is desired, for example to raise strength and operating temperature, PCTG and PEKK can be thermally annealed in a controlled process to allow the crystalline regions to grow. A higher degree of crystallinity gives the plastic higher strength and stiffness, but it reduces the material ductility.

Mechanical Properties

Another key difference between amorphous and semi-crystalline plastics is their mechanical behavior with temperature. As the temperature is raised, the stiffness of amorphous plastics

decreases slowly until T_g is reached, then the stiffness drops quickly as the polymer enters the viscoelastic melt state. Semi-crystalline polymers also experience a loss in stiffness above T_g which continues to decrease steadily up to T_m ; however, within that range, they retain enough stiffness to be mechanically functional in many applications (consider HDPE whitewater kayaks) due to the integrity of the crystalline regions. Above T_m , the stiffness almost immediately vanishes as the polymer enters the viscoelastic melt state.

Fiber fillers in semicrystalline plastics can greatly improve these behaviors. Fibers raise the stiffness of both amorphous and semi-crystalline polymers. For example, check our technical datasheets to see the difference in elastic tensile modulus between Essentium's polyamide (PA) and polyamide carbon fiber (PA-CF) materials: 1.95 GPa compared to 3.45 GPa with the addition of fibers. However the temperature performance of semi-crystalline polymers benefits the most from the inclusion of fiber reinforcements.

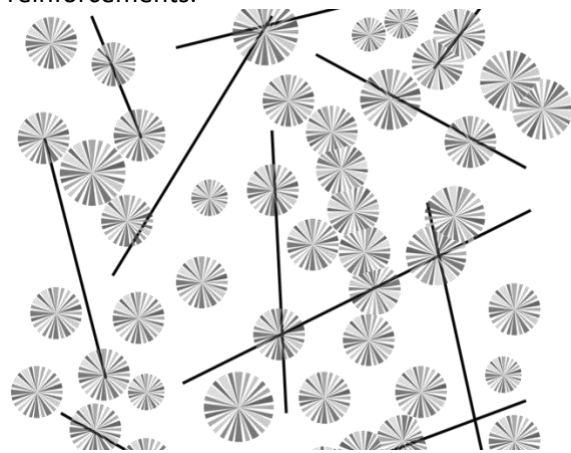


Figure 6. Illustration of fiber reinforcements linking together semi-crystalline domains in a polymer.

This is due to the way crystalline domains nucleate along fibers and become linked together by the stiffness of the fiber (Figure 6). The amorphous regions between the crystalline domains and tie chains between lamellae no longer dominate the thermomechanical properties above the T_g . Fiber reinforced semi-crystalline polymers also have outstanding creep resistance above their T_g compared to their neat base resins. Amorphous polymers do not typically benefit from the addition of fiber reinforcements above their T_g . Figure 7 shows a schematic representation of the flexural stiffness of polymers with increasing temperature, typically measured with a technique called dynamic mechanical analysis (DMA).

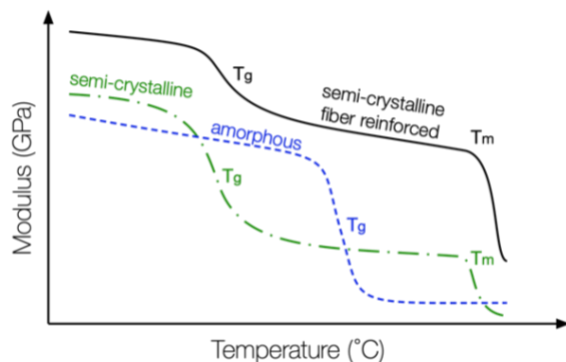


Figure 7. Illustrative dynamic mechanical analysis (DMA) curve for amorphous, semi-crystalline, and fiber-filled semi-crystalline plastics.

Related to this behavior is a metric called heat deflection temperature (HDT), which is the temperature at which a polymer sample deforms a specified amount under a predetermined load. It does not completely capture the complex mechanical behavior of thermoplastics, but it is a single point value useful for comparison between different grades. Table 2 gives the HDT for several common plastics. The effect of fibers is striking with PEEK and glass-filled PEEK.

Table 2. HDT for some common plastics. Adapted from Baur, Osswald, and Rudolph, *Plastics Handbook*, Hanser, 2019, and *Matweb, www.matweb.com.

	Abbr.	HDT [°C] 1.8 MPa ISO 75A
High Density Polyethylene	HDPE	50
Polypropylene	PP	62
Polystyrene	PS	75
Polycarbonate	PC	130
Acrylonitrile Butadiene Styrene	ABS	100
Polyethylene Terephthalate Glycol	PETG	72*
Poly Cyclohexylenedimethylene Terephthalate Glycol	PCTG	66*
Polyphenylsulfone	PPSU	200*
Polyetherimide	PEI	195
Polyether ether ketone	PEEK	140
PEEK with 30% Glass Fiber	PEEK	315
Polyether ketone ketone	PEKK	158*

Other Functional Properties

The molecular structure of plastics explains key differences in other functional properties as well. The unordered nature of amorphous materials allows for higher molecular mobility, which gives these materials higher impact resistance. Bullet-proof 'glass,' after all, is the amorphous polymer polycarbonate (PC). Many interior car parts are made of amorphous ABS, which resists the bumps and bangs of years of use. However, not all amorphous polymers have this property. For example, poly(methyl methacrylate) (PMMA), also known as acrylic or plexiglass, is used as a glass substitute, and polystyrene (PS), is used in things like CD cases and disposable plastic cutlery. Both are very brittle. On the other hand, HDPE can be very

impact resistant – again, think whitewater kayaks, large trash bins, and plastic shopping carts. The reasons for these differences are complex, but they are related to the mechanisms for crack formation in the different materials.

Finally, the chemical resistance of amorphous plastics is generally lower than that of semi-crystalline plastics. Because the crystalline regions are so dense and the molecules are tightly packed, it is more difficult for chemicals to penetrate the network. For the same reason, semi-crystalline polymers such as polyethylene, polypropylene, and ethylene vinyl alcohol (EVOH) are used in food packaging – they have low permeability for water (PE/PP) and oxygen (EVOH). It is important to note, however, that chemicals and solvents will interact in different ways with different polymers, and the presence of residual stresses or external loads can make a polymer more susceptible to chemical attack, leading to an effect called environmental stress cracking. Therefore, it's essential to look at the compatibility of particular chemical/polymer systems or conduct representative testing in order to choose the right polymer for the right application.