



TECHNICAL NEWSLETTER

Crystallinity in Plastics

Introduction

In previous Technical Newsletters, we mentioned the effect of crystallinity in plastics but never delved deeper into this topic. This Technical Newsletter will more closely consider crystallinity in plastics: what it is, and more importantly, how it affects the properties of plastics.

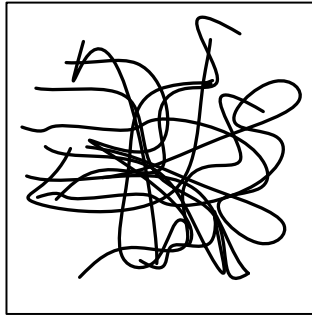
Most people are familiar with crystals only because of salt and perhaps growing crystals as part of a school science project. Therefore, talking about crystals and plastics together is a new concept to many people. In reality, polymers are not like salt, which is totally crystalline, but are semi-crystalline. Unlike crystals like salt, polymers have only short-range order and a much looser organization.

Crystallinity is one of the great divisions of the complete family of plastics. Amorphous polymers (those with no significant degree of crystallization) behave very differently than crystalline polymers (those with a significant degree of crystallization). Understanding crystallization and the effect it has on the properties of polymers can make understanding the behavior of polymer families much easier.

Amorphous and crystalline polymers:

Amorphous polymers

Amorphous polymers are those where the polymer chains have no well-defined order in either the solid or liquid states. The model that is most often associated with this characterization is a bowl of cooked spaghetti, where the long strands of spaghetti are both flexible and slide over one another. This is similar to a molten amorphous polymer as it is being processed. If the hot spaghetti is tipped into a bowl, then it will take the shape of the bowl, just as a plastic does when it fills a mold. After the spaghetti has cooled, the long strands tend to stick to one another, which is very similar to the behavior of an amorphous polymer after it has cooled. The classic two-dimensional representation of an amorphous polymer is shown below:

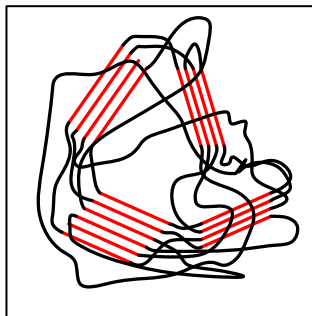


Amorphous polymer - random molecular orientation in both molten and solid phases

Examples of amorphous polymer are PMMA, PS, PVC and ABS. As a rule, any polymer that can be produced in a transparent form is an amorphous polymer.

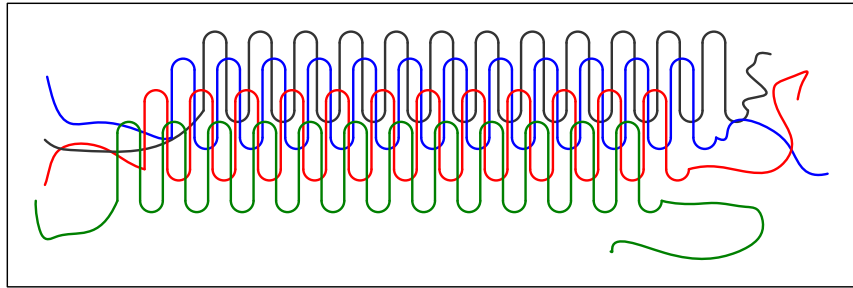
Crystalline polymers

In the molten phase, crystalline polymers closely resemble amorphous polymers. However, the real difference between the two exhibits itself during cooling. As crystalline polymers cool, small areas of short-range order form. These are highly organized and closely packed areas of polymer molecules and are recognized as the “polymer crystals” in crystalline polymers. However, they are not at all like the crystals in salt or other inorganic materials. There are several models and theories regarding crystal formation, but the most popular is the “fringed micelle” model. Shown below is a two-dimensional representation of molecules in a crystalline polymer according to the fringed micelle theory. It shows the ordered regions or crystallites (in red) embedded in an amorphous matrix.



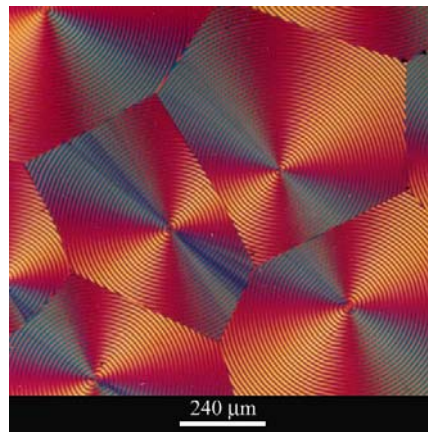
Crystalline polymer - random molecular orientation in molten phase but densely packed crystallites in solid phase

The red ordered regions show above are made up of polymer chains that are folded into highly ordered regions as shown in the figure below.



Folded lamellae crystals in a crystalline polymer, color coded for clarity.

A single polymer backbone chain may be present in sections of different crystallites, which are generally small and separated by areas without a short-range order. Larger structures, made up of bundles of crystallites, are termed spherulites and these are formed in the bulk of the material. These are formed and grow in a similar manner to the formation and growth of grains in a metal.



Spherulites in poly-3-hydroxy butyrate (PHB)

Source: Prof T. W. Clyne, Department of Materials Science and Metallurgy, University of Cambridge, UK. Used with permission. This image (with full documentation) is available at www.msm.cam.ac.uk/doitpoms/miclib

Crystal formation begins at nucleation points and extends outwards into the bulk of the polymer. The nucleation itself can be one of the following:

- Homogeneous - this is the case for a pure polymer, e.g. virgin PP and the result is a small number nucleation sites and a few large crystals as seen in the figure above.
- Heterogeneous - where particles in the polymer (natural or added deliberately) act as nucleation sites and many small crystals are formed. This is the case for PP with certain coloring agents and results in higher shrinkage rates.

The type of nucleation process will also affect the properties of crystalline polymers. A product with relatively few large crystals will have different properties than one with more, but smaller, crystals.

Examples of crystalline polymers are PP, PE (all varieties but some more so than others), PA and POM. As a rule, any polymer that is translucent or opaque in the natural form is a crystalline polymer.

The degree of crystallinity

Not all polymers crystallize to the same degree. All polymers have some degree of crystallinity except for amorphous polymers. Crystallinity can vary between 0% (an amorphous polymer) and 80% (a highly crystalline polymer).

There are also a number of variables present in polymer structure that affect crystallinity, and they are:

- **Polymer chain length:** Molecular weight is a measure of how long the polymer backbone chain is. If the molecular weight is high, then the polymer backbone chain is long and the degree of crystallinity is reduced. This is illustrated by the behavior of PE. HDPE molecules are up to 100 times longer than LDPE molecules. As a result, the degree of crystallinity of HDPE is much lower than LDPE.
- **Stereoregularity:** This is a measure of how the mers (the repeat units in the polymer) are arranged in the polymer backbone chain. Isotactic materials have the mers connected together in a single repeated manner, syndiotactic materials have the mers connected together in a regularly repeated but different manner, and atactic materials have the mers connected together in a random manner. Atactic materials are generally amorphous because of the lack of polymer chain order, whereas isotactic and syndiotactic polymers are typically crystalline because of the high degree of polymer chain regularity. This effect can be used to increase the properties of some polymer, such as PP, by encouraging crystallization through the use of stereospecific forms of the material.
- **Polar groups:** Some polymers have polar groups present along the main polymer chain, e.g. the CO group is present in many amorphous polymers. These groups repel each other and prevent the formation of crystalline structures. Equally, some materials, such as the polyamides, form crystals very easily because of the attraction between sections of the main backbone chain.
- **Chain branching:** The degree of branching on the main backbone chain will affect the ability to crystallize. Highly branched polymers will generally be less crystalline than linear polymers due to the presence of long branches.

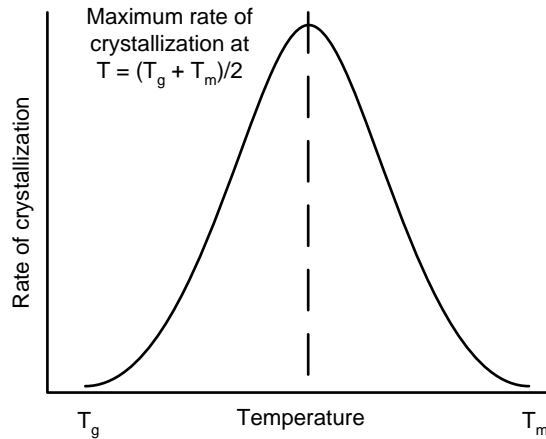
The rate of crystallization

The rate of crystallization is dependent on temperature, of which there are two significant points:

- **T_g** - The glass transition temperature. Below T_g, there is virtually no molecular motion on a local scale. Polymers have many of the properties associated with ordinary organic glasses including hardness and stiffness.

- T_m - The crystalline melting point. This is the temperature at which crystals melt and a crystalline polymer resembles an amorphous polymer, which has no short-range order. T_m generally increases as the degree of crystallinity increases.

The rate of crystallization (both nucleation and growth) depends on temperature, as shown below:



Typical form of crystallization rate-temperature curve for a crystalline linear polymer

Above T_m , no crystallization exists and below T_g , no further movement of molecules is possible to nucleate or grow crystals. The fastest rate of crystallization occurs midway between T_g and T_m . The longer a polymer remains between the two, the greater the amount of crystallization. For example:

- For PP, T_g is -10 to -20°C and T_m is 150 to 175°C – PP will therefore continue to crystallize slowly at room temperature (21°C) until equilibrium is reached.
- For PTFE, T_g is -110°C and T_m 330°C – PTFE crystallizes rapidly at room temperature (21°C).

The properties of amorphous and crystalline polymers:

General properties

The general properties of amorphous and crystalline polymers are shown below:

GENERAL PROPERTIES	
AMORPHOUS PLASTICS	SEMI-CRYSTALLINE PLASTICS
<ul style="list-style-type: none"> ▪ Soften over a wide range of temperatures ▪ Lower specific gravity ▪ Lower tensile strength and tensile modulus ▪ Higher ductility and impact strength ▪ Lower creep resistance 	<ul style="list-style-type: none"> ▪ Distinct and sharp melting point ▪ Higher specific gravity due to better packing ▪ Higher tensile strength and tensile modulus ▪ Lower ductility and impact strength

<ul style="list-style-type: none"> ▪ Tend to be transparent ▪ Higher dimensional stability ▪ Lower fatigue resistance ▪ Bond well using adhesives and solvents ▪ Lower chemical resistance and resistance to stress cracking ▪ Structural applications only (not for bearing and wear) 	<ul style="list-style-type: none"> ▪ Higher creep resistance ▪ Tend to be translucent or opaque ▪ Lower dimensional stability ▪ Higher fatigue resistance ▪ Difficult to bond using adhesives and solvents ▪ Higher chemical resistance and resistance to stress cracking ▪ Good for bearing and wear, as well as for structural applications
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The general properties of amorphous and crystalline polymers

Simply knowing if a polymer is amorphous or crystalline will help define its behavior and many of its properties. The Periodic Table of Thermoplastics (developed by Tangram Technology Ltd.) depicts how the distinction between amorphous and crystalline polymers represents one of the fundamental divisions in the thermoplastics family. It is shown on the following page.

Melting behavior

Crystalline polymers have distinct melting points (T_m). At this point, the crystalline regions break up and short-range order is lost. However, in amorphous polymers, regions tend to soften over a wide temperature range.

Shrinkage¹

Shrinkage of plastics products after processing is common, but crystalline and amorphous polymers shrink differently. All plastics parts shrink after processing simply as a result of their compressibility and the thermal contraction as they cool from the processing temperature. With amorphous plastics, this is the only factor and is easily calculated. But because crystallites contain more ordered and better packing of the polymer chains, phase transition increases shrinkage considerably.

For amorphous polymers, shrinkage values are not only low, but shrinkage itself is quick to occur. For a typical amorphous polymer such as PMMA, the shrinkage will be in the order of 0.001 - 0.005 m/m. This is due to cooling from about 150°C (the temperature of the melt) to 23°C (room temperature) and can be related to the co-efficient of thermal expansion. Shrinkage is 90-95% complete immediately after processing and 100% complete within 3 to 4 hours².

Crystalline polymers are not only affected by compressibility and temperature shrinkage but also by crystallization shrinkage. As the polymer solidifies, crystals form and the improved packing leads to shrinkage values far greater than those seen in amorphous polymers. For a typical crystalline polymer such as PP, shrinkage will be in the order of 0.01 - 0.025 m/m. This is between 5 to 10 times the shrinkage of an amorphous polymer. Only about 85% of this higher shrinkage will have taken place in the first 24 hours, about 98-99% will have taken place in the first week and the remaining shrinkage may take up to 3 months to complete.

Generally, about 85% of shrinkage occurs in the first 24 hours and 98-99% has taken place in the first week. The remaining shrinkage may take up to 3 months to complete. In such cases, it is normal to anneal the molded article for a short time at the maximum crystallization temperature to force the polymer to equilibrium where full shrinkage can take place within an hour.

This variable shrinkage effect means that processing tolerances achievable for amorphous polymers are far better than those for crystalline polymers.

¹ For a more complete discussion of shrinkage in plastics parts see: www.tangram.co.uk/TI-Polymer-Shrinkage_in_plastics.html

² Other factors, such as part geometry, orientation and molding parameters have been ignored in this simple explanation.

Controlling crystallinity

Crystallinity can be controlled, even in semi-crystalline plastics by modifying processing techniques. It is possible to quench, or rapidly cool, plastic parts to reduce the formation of crystals. However, the success of this depends on the relationship of T_g (the glass transition temperature) of the polymer and the service temperature. If T_g is higher than the service temperature, then the quenching will prevent the formation of crystals during cooling. As a result, they are unlikely to form during the service life of the product. Equally, if the service temperature is approximately the same as or higher than T_g , then quenching will only delay the inevitable, and crystallization and shrinkage will eventually occur down the road, possibly making the product unfit for use.

Equally, it is possible to anneal polymers after processing to ensure that proper crystallization has taken place. Annealing involves holding the polymer above T_g but below T_m for a specific time to both encourage and control the growth of the crystalline structure.

High nucleation and growth rates can also be achieved if heterogeneous nucleation is used. In this case, nucleation is initiated by seeding with a foreign particle, which is typically a polymer similar to the base polymer but with a higher melting point. Some commercial products incorporate special nucleating agents to produce a high degree of crystallization and controlled structures, including coloring agents.

It is also possible to induce directional crystallization by stretching polymers below T_m to create crystalline filaments, fibers or sheets with a crystalline structure oriented in the direction of stretching. This cold-drawing technique is used extensively in fiber and film production to produce high strength fibers and films and in the production of PET bottles with injection blow molding.

Summary

Crystallinity in polymers is not a simple laboratory curiosity or topic of marginal interest. It is one of the fundamental divisions between polymer types and it both controls and affects many of the polymer processing techniques that are in common use today. Understanding crystallization is not difficult and once understood it provides a framework for understanding many of the properties, processes and problems of modern plastics processing.

At Zeus, we deal with highly crystalline materials every day. With over 40 years of experience working with products like PTFE, FEP, PFA, and PEEK, we have the expert scientists and technical design engineers able to meet your needs and address your concerns.