



Plastics Topics – Crystallinity and plastics

**TANGRAM
TECHNOLOGY**

**Consulting
Engineers**

Tangram Technology Ltd.
33 Gaping Lane, Hitchin, Herts., SG5 2DF

Phone: 01462 437 686

E-mail: sales@tangram.co.uk

Web Pages: www.tangram.co.uk

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Plastics Topics – Crystallinity and plastics

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1. Introduction

In several of the Plastics Topics we have mentioned the effect of crystallinity in plastics in passing but have never delved deeper into this fascinating topic. This document considers crystallinity in plastics – what it is and more importantly how it dramatically affects the properties of plastics.

Most people are familiar with crystals if only through the common crystals such as salt and even perhaps through growing crystals as part of a school science project. Talking about crystals and plastics therefore comes as a surprise to many people who associate crystals with regularly shaped solids and not with plastics. In reality polymers are not like salt, which is totally crystalline, but are semi-crystalline in that they do not have the highly organized long-range order of salt but instead 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 to 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 behaviour of whole families of polymers much easier. Understanding crystallinity is truly vital to understanding the behaviour of polymers.

2. 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 and the model that is often used is that of a bowl of cooked spaghetti. In a bowl of freshly cooked hot and wet spaghetti, 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 up the shape of the bowl, just as a plastic does when it fills a mould. After the spaghetti has cooled the long strands tend to stick to one another and also resemble an amorphous polymer after it has cooled. At this stage if the spaghetti is removed from the bowl, then it will tend to retain the shape of the bowl, just as a plastic does when it is removed from a mould.

The classic two-dimensional representation of an amorphous polymer is shown in Figure 1:

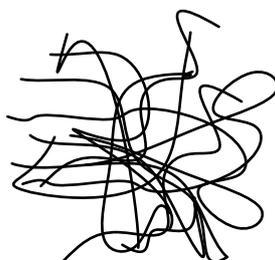


Figure 1: Amorphous polymer – random molecular orientation in both molten and solid phases.

Examples of amorphous polymers 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

Crystalline polymers resemble amorphous polymers when in the molten phase. The real difference from amorphous polymers comes 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 the 'polymer crystals' in crystalline polymers. They are not at all like the crystals in salt or other inorganic materials. There are several models and theories for the crystal formation but the most popular involves a 'fringed micelle' model. The classic two-dimensional representation of a crystalline polymer is shown in Figure 2. This is a two-dimensional representation of molecules in a crystalline polymer according to the fringed micelle theory showing ordered regions or crystallites (in red) embedded in an amorphous matrix.

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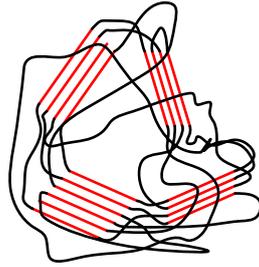


Figure 2: Crystalline polymer – random molecular orientation in molten phase but densely packed crystallites in solid phase.

The red ordered regions in Figure 2 are made up of polymer chains that are folded into highly ordered regions as shown in Figure 3:

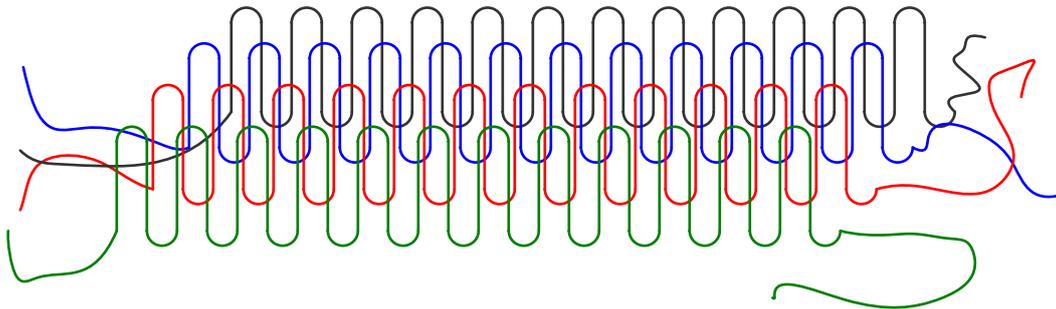


Figure 3: Folded lamellae (plate-like) crystals in a crystalline polymer. Colour coded only for clarity.

A single polymer backbone chain may be involved in several sections of different crystallites and the lamellae are not made up of a single discrete chain. The crystalline sections are generally small and separated by areas of no short-range order, the amorphous regions of Figure 2, and in the three-dimensional case there are no well-defined boundaries between the crystalline and the amorphous regions.

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.

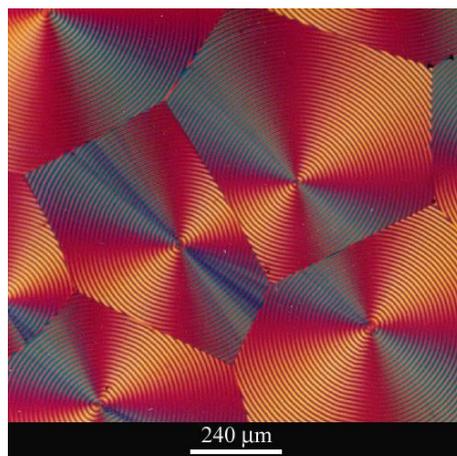


Figure 4: Spherulites in poly-3-hydroxy butyrate (PHB)

**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**

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Crystal formation begins at nucleation points and extends outwards into the bulk of the polymer. The nucleation itself can be either homogeneous or heterogeneous:

- Homogeneous nucleation - 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 Figure 4.
- Heterogeneous nucleation - 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 colouring 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 very different properties to 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 and crystallinity is really a percentage game, i.e., all polymers can be considered to have some 'degree of crystallinity' but the degree of crystallinity is simply zero for amorphous polymers. The degree of crystallinity can therefore vary between 0% (an amorphous polymer) to an upper limit if approximately 80% (a very highly crystalline polymer).

The degree of crystallinity affects the properties of polymers and it is sensitive to a range of important variables in polymer structure – structure always influences properties. Some of the variables in polymer structure that affect crystallinity 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 generally reduced. This is illustrated by the behaviour of PE; HDPE molecules are up to 100 times longer than LDPE molecules and the result is that the degree of crystallinity of HDPE is typically much lower than that of 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 totally random manner. Atactic materials are generally amorphous because of their lack of order in polymer chain whereas isotactic and syndiotactic polymers are generally crystalline because of the high degree of regularity in the main polymer chain. 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 highly polar groups present along the main polymer chain (e.g., the CO group is present in many amorphous polymers). These groups repel one another and prevent the formation of crystalline structures. Equally, some materials (e.g., the polyamides) form crystals very easily because of the attractions between sections of the main backbone chain.
- Chain branching: The degree of branching on the main backbone chain will affect the ability to crystallize and highly branched polymers will generally be less crystalline than strongly linear polymers due to the presence of the long branches.

The rate of crystallization

The rate of crystallization is dependent on temperature and there are two critical temperatures:

- T_g – The glass transition temperature: Below T_g there is virtually no molecular motion on a local scale and 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, i.e., 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 in Figure 5:

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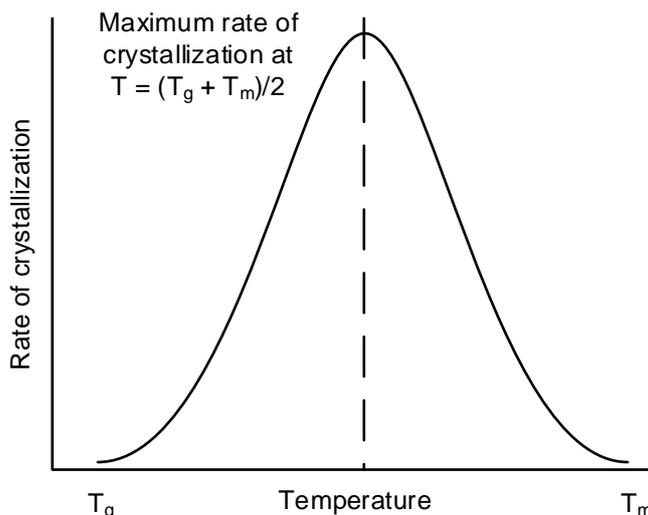


Figure 5: Typical form of crystallization rate-temperature curve for a crystalline linear polymer.

Above T_m no crystallization exists (by definition of T_m) 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 and the longer that a polymer remains between T_g and T_m the greater will be the amount of crystallization. As examples:

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

3. The properties of amorphous and crystalline polymers

General properties

The general properties of amorphous and crystalline polymers are shown in Figure 6:

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. • 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"> • Distinct and sharp melting point. • Higher specific gravity due to better packing. • Higher tensile strength and tensile modulus. • Lower ductility and impact strength. • 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.

Figure 6: The general properties of amorphous and crystalline polymers

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Simply knowing if a polymer is amorphous or crystalline will help to define many of the properties and behaviour of the polymer. Understanding crystallinity is truly vital to understanding the behaviour of polymers. The Periodic Table of Thermoplastics (developed by Tangram Technology Ltd.) uses the distinction between amorphous and crystalline polymers as one of the fundamental divisions in the complete family of thermoplastics and is shown in Figure 7 for reference:

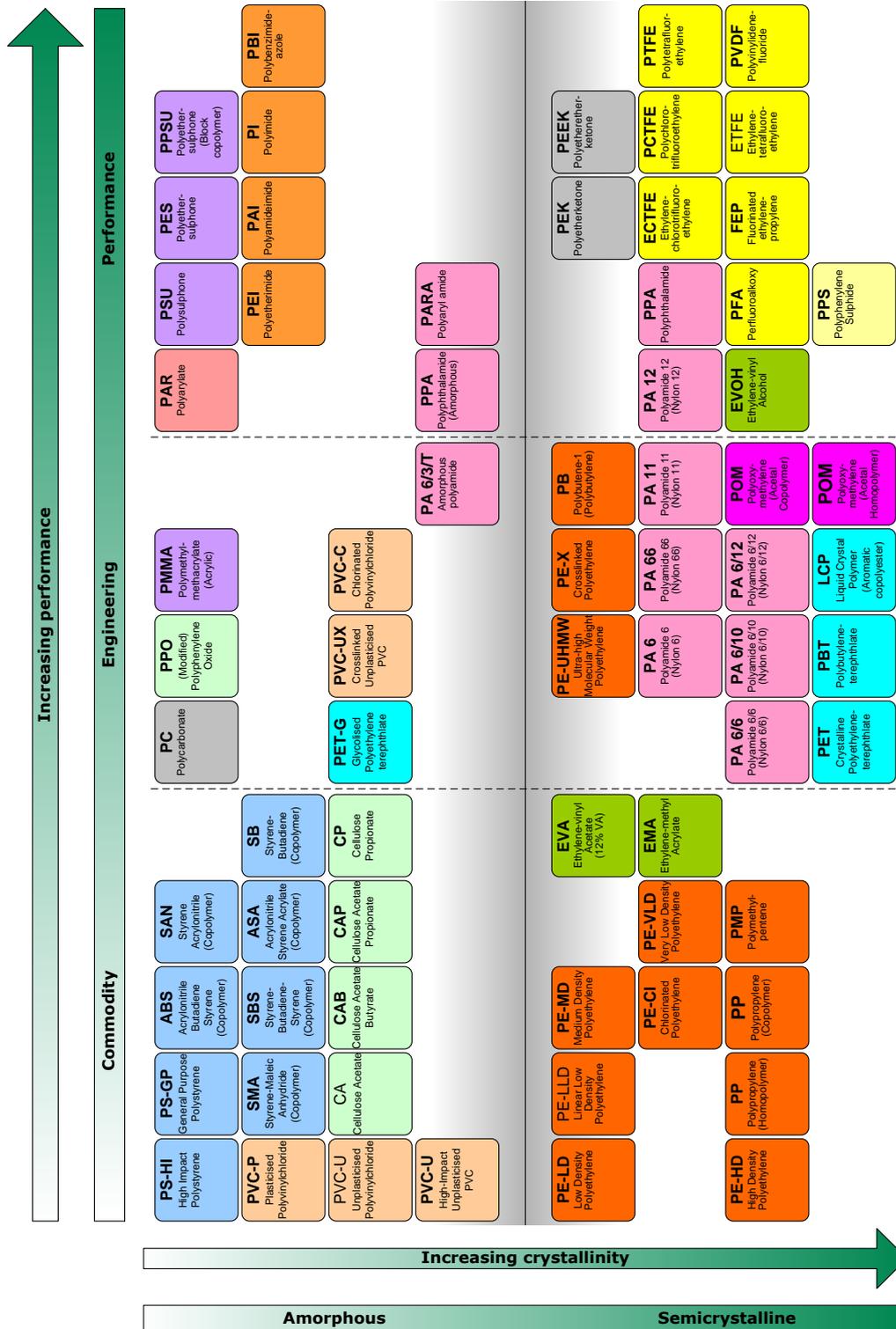


Figure 7: Amorphous and crystalline plastics
 Adapted from 'The Periodic Table of Thermoplastics'
 Tangram Technology Ltd. (www.tangram.co.uk)

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Melting behaviour

Crystalline polymers have true and distinct melting points (T_m) when the crystalline regions break up and short-range order is lost whereas amorphous polymers tend to soften over a relatively wide temperature range in the region of T_g .

Shrinkage¹

Shrinkage of plastics products after processing is common for all plastics but crystalline and amorphous polymers behave somewhat 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 relatively easily calculated. With crystalline plastics, the phase transition as crystallization takes place in the crystalline portion of the material increases the shrinkage considerably as the crystallites have more ordered and better packing of the polymer chains and hence increased shrinkage.

For amorphous polymers, shrinkage values are not only low but also shrinkage is relatively fast. For a typical amorphous polymer such as PMMA, the shrinkage will be in the order of 0.001 - 0.005 m/m. This shrinkage is simply 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. The 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, the 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 moulded 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 high and somewhat variable shrinkage effect means that the processing tolerances achievable for amorphous polymers are far better than those achievable for crystalline polymers.

4. Controlling crystallinity

Crystallinity can be controlled, even in semi-crystalline plastics by modifying processing techniques.

It is possible to 'quench' (rapidly cool) plastic parts to reduce the formation of crystals during cooling from the process temperature but the success of this depends on the relationship of T_g (the glass transition temperature) of the polymer to the service temperature. If T_g is much higher than the service temperature then the quenching will prevent the formation of crystals during cooling and 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 during service and possibly make the product unfit for purpose.

Equally it is possible to anneal polymers after processing to ensure that crystallization has taken place to the required degree. 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, frequently a polymer similar to the base polymer but with a higher melting point. Some commercial products incorporate special nucleating

¹ For a more complete discussion of shrinkage in plastics parts see the Plastics Topics - Shrinkage in plastics processing.

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

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agents to give a high degree of crystallization and controlled structures. In some cases, the presence of a colorant can act as a nucleation agent and create different crystallization and shrinkage for different colours. This is not a pleasant effect to try to resolve!

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

5. 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.