

# Crystallization and nucleation of semi-crystalline polymers

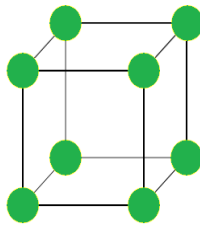
Carmine Di Fiore 24 July 2014

A small review on what is a crystal, what is a semi-crystalline polymer, what is the influence of nucleating agents on the crystallization process of polymers. And a non-exhaustive list of which are the commercial available nucleating agents.

The crystallization is a physical phenomenon during which atoms or molecules and / or ions are arranged in space in a precise and repetitive way. A crystal (from the Greek *Krystallos*, *Kryos =ice*) is therefore a solid object consisting of atoms, molecules and / or ions having a geometrically regular disposition that is repeated indefinitely in the three space dimensions, called the crystal lattice. The presence of this atomic organization gives to the crystal a definite geometric shape.

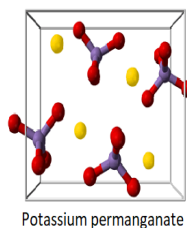
## The unit cell

is the smallest part of a crystal that is repeated regularly through translation in three dimensions creates the whole crystal. For example, the image shown here is the unit cell of a primitive cubic structure. In the structure drawn, all of the particles (green) are the same. In this particular case, the lattice points defining the unit cell coincide with the centers of the crystal's particles. This need not always be the case.



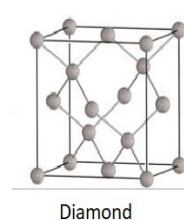
## The Ionic Lattice

If a crystal is formed of ions, the compound can be described as an ionic lattice. Well-known examples of ionic lattices are sodium chloride, potassium permanganate, borax (sodium borate) and copper(II) sulfate.



## The Covalent Lattice

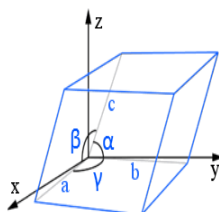
If a crystal is made up of covalently bonded atoms, it can be described as a covalent lattice or infinite covalent lattice. Well-known examples of covalent lattices are diamond, quartz (silicon dioxide), silicon, and grey tin, diamond.



## Lattice Constants

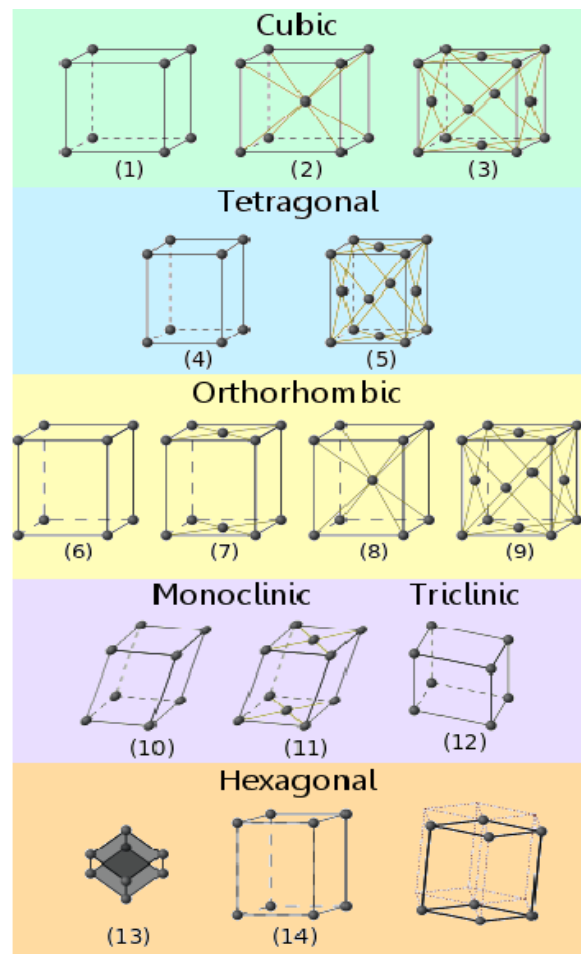
The lattice constants (or lattice parameters) are the lengths and the angles between of the edges of the unit cell.

In this parallelepiped are show, the lattice constants are  $a$ ,  $b$ , and  $c$  (lengths) and  $\alpha$ ,  $\beta$ , and  $\gamma$  (angles).



## Lattice Structures

Crystalline materials fit into one of fourteen recognized lattice arrangements. These are known as **Bravais lattices**. The names of the crystal lattice systems, corresponding to the numbers on the diagrams, are as follows:



## Reticoli Cristallini

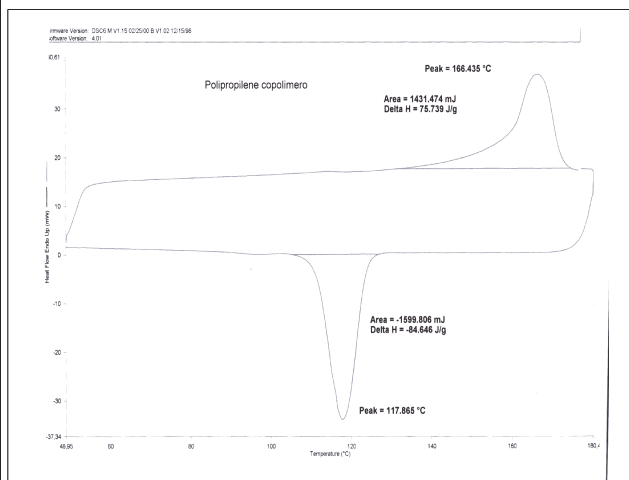
- |                               |                               |
|-------------------------------|-------------------------------|
| 1. Primitive cubic            | 8. Body centered Orthorhombic |
| 2. Body centered cubic        | 9. Face centered Orthorhombic |
| 3. Face centered cubic        | 10. Primitive monoclinic      |
| 4. Primitive tetragonal       | 11. Base centered monoclinic  |
| 5. Body centered tetragonal   | 12. Triclinic                 |
| 6. Primitive orthorhombic     | 13. Rhombohedral              |
| 7. Base centered orthorhombic | 14. Hexagonal                 |

## Lattice Defects

If a crystal were assumed to be based on a mathematically perfect ionic lattice, its calculated tensile strength would be much greater than is actually observed. Real crystals have lattice defects that are sources of weakness. Ions missing from their expected locations and ions occupying unusual coordination sites are examples of lattice defects. Lattice defects can also be beneficial effect, improving the conductivity of some semiconductor materials, for example.

In practice, the crystallization process is a particular change in the state of matter which can occur from liquid to solid (solidification), from gas to solid (condensation), or even under certain conditions of temperature and pressure for irradiation of atoms in the glass phase. In all cases the temperature change plays a decisive role. If the temperature reduction is too fast, the atoms or molecules and / or ions do not have the time to arrange themselves in an orderly way in space and tend to form what is called an amorphous solid or glass. Even the pressure plays a decisive role but only at very high values therefore we will not take it into account later in the discussion.

Things become more complex if the molecule (or ion), that crystallizes, is not formed by a few atoms but if it is a macromolecule: a polymer (eg Polypropylene). In fact, for small molecules (eg. Water) the crystallization temperature is practically the same as the melting temperature (from 0 ° C to 1 atm). This is not equally true for a polymer, such as polypropylene, which can remain at a lower temperature than the melting temperature for a relatively long time. That is, until, within the molten mass, small variations in concentration in the sub-cooled and supersaturated areas start the formation of germs (nuclei) around which the crystalline phase develops.

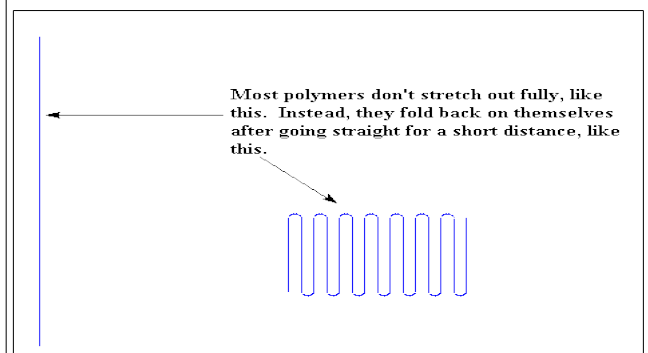


This phase transformation is normally caused by the temperature reduction and is usually described in terms of nucleation and subsequent growth of the crystalline phase. This phenomenon is graphically reported by the following DSC (differential scanning calorimetry) diagram, in which it is seen that the melting point of the specific polypropylene is 166 ° C and that the point of crystallization (or rather of partial crystallization being a semicrystalline material ) is 117 ° C. This value is obtained by cooling the sample from the melt at a rate of 10 ° C per minute. In order for a polymer to crystallize, the following conditions must be met:

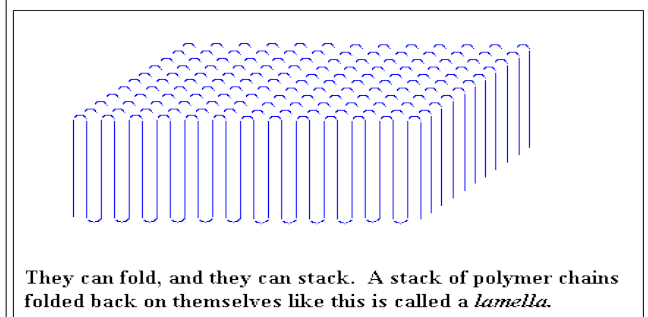
- The molecular structure of the polymer must be sufficiently regular to allow the formation of ordered crystals.
- The crystallization temperature must be lower than the melting temperature but not too close to the polymer glass transition temperature.
- A nucleation process prior to crystallization must take place.
- The crystallization rate must be sufficiently high.

The explanation of all this is to be found in the difficulty of the polymer chains to find the right position to form the crystals. This is why the crystallization usually occurs at a much lower temperature than the melting point during cooling.

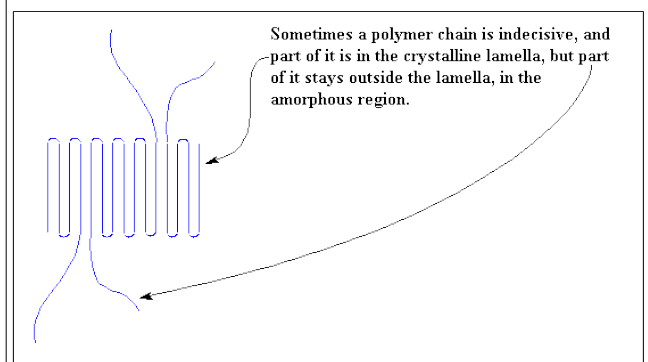
The polymeric chains, due to their length, do not generally manage to stretch out completely and therefore tend to fold back on themselves in order to crystallize and order themselves as follows:



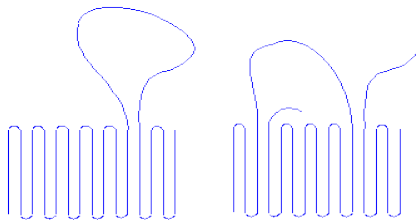
Ideally we should have a lamellar structure so formed:



However, what actually happens is that the molecular chains do not succeed in disposing in such a regular way, in fact, situations occur such as those depicted by the two following images:



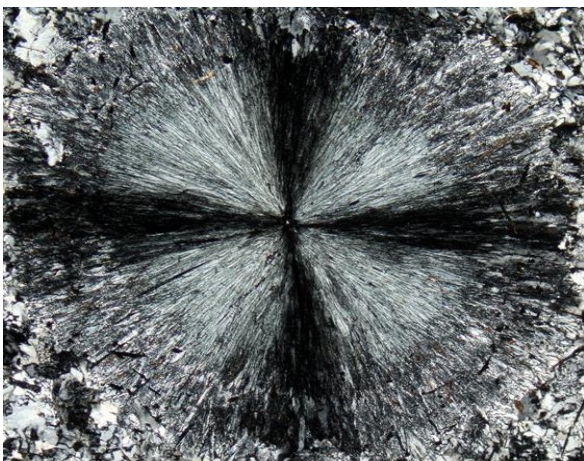
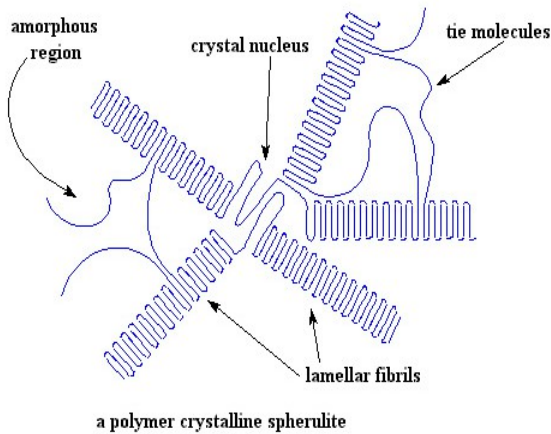
Sometimes a polymeric chain is undecided, a part is in the crystalline lamella, but another part remains outside, in the amorphous region.



These lamellae have chains that go out for awhile, then come back in. On the left, the chain re-enters the lamellae right next to where it left. On the right our outgoing chain comes back in some distance away from where it left. Both are possible. These two pictures both show what is called the *switchboard model* of a polymer crystalline lamella.

These lamellae have chains that come out for a while then return. On the left the chain re-enters in the lamellae right next to where it came out. In the figure on the right the spilled chain returns to a point far from where it came out. These are two possible cases. Both figures show the so-called "switchboard" model of a crystalline polymeric lamella.

These processes originate from a crystallization nucleus around which a three-dimensional structure called spherulite is created which can be represented more or less as follows:

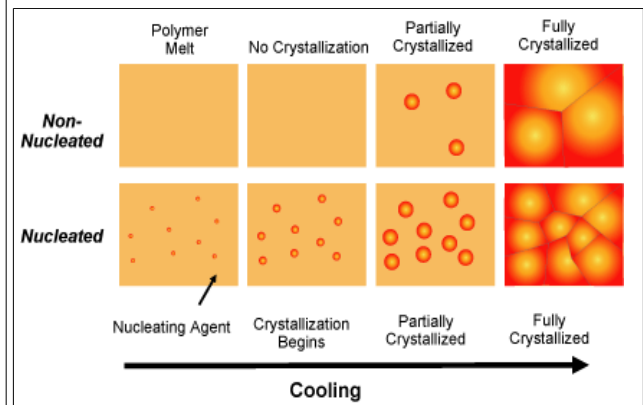


At this point it appears evident in the crystallization process that two distinct regions are formed: one properly called crystalline and one in which the chains remain disordered, amorphous regions. (from the ratio of the two different regions there is the degree of crystallinity, eg PEHD has a degree of crystallinity of about 80% isotactic polypropylene, a degree of crystallinity of about 63% ...) This is the reason why we talk about semi-crystalline materials.

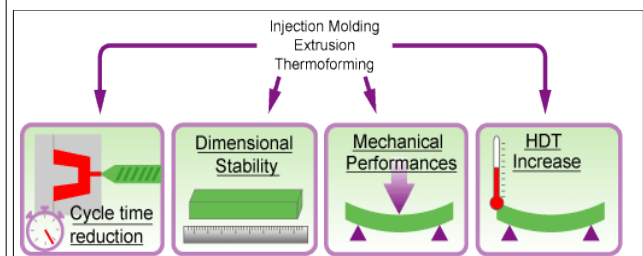
The percentage of crystallinity in the finished product can vary significantly depending on a series of circumstances: cooling rate, pressures, presence of nucleating agents, etc. ... Precisely about the changes induced in the crystallization process by the presence of nucleating agents is the topic we want to deal with now.

### Operation mechanism

The working mechanism of the nucleating agents can be better understood by looking at the next figure. In practice, a good nucleating agent favors the formation of crystalline nuclei at a higher temperature than that normally formed in the molten polymer thus promoting both the crystallization at higher temperatures than those of the pure polymer and the formation of smaller crystals and finally also a higher percentage of crystallinity.

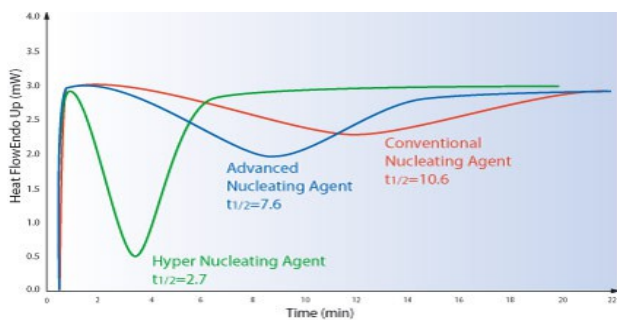


A faster crystallization rate favors greater productivity in injection molding and extrusion processes. The total percentage of crystallinity of the polymer improves the mechanical characteristics and the 'HDT (heat distortion temperature).



The difference between the crystallization temperature of the non-additivated and the additivated material is more marked the more efficient the nucleating agent is.

In addition to the reduction of the crystallization temperature, the isothermal crystallization time can be evaluated by DSC.



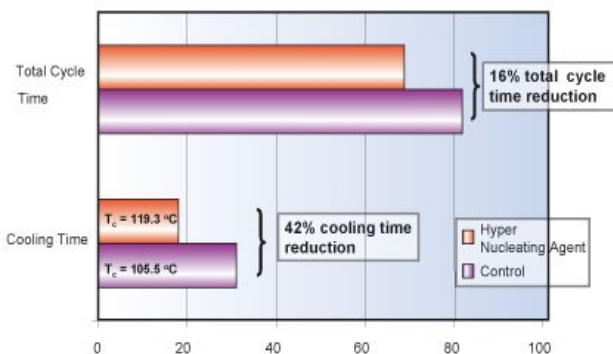
### A practical example

By increasing the crystallization temperature in the injection molding cycles there is a reduction in the solidification times of the molded part thus favoring the total reduction of the process time. For example, the molding of a chair using a modified high impact resistance homopolymer blend has that the total molding time is 82 seconds using a non-nucleated material.



Most of this time is that necessary for cooling the piece

"cooling time" in the mold; necessary to have the dimensional stability of the piece and the degree of crystallinity necessary for this application. The addition of a suitable nucleating agent reduces the cooling time by 42% and the total cycle time by 16%.



The addition of the nucleating agent led to a reduction of the total time of the molding cycle by 16%, compared to the reference time. In practice, the increase in the crystallization temperature due to the nuclear agent makes it possible to remove the molded piece first from the mold. With obvious repercussions on costs (more pieces in less time).

### Nucleating agents

The nucleating agents commercially available can be divided into two groups, generally defined "melt sensitive" and "melt insensitive".

The melt sensitive nucleants have a melting point which is below or near the normal processing temperature of modified polymer; while the melt insensitive are not melting at the normal processing temperatures. Melt sensitive nucleants include additives based on sorbitol, which provide also an enhancement of clarity and, because of this property, they are called "clarifiers". PP compounds with this kind of additives are very sensitive to the processing temperatures, being sorbitol derivatives unstable at high temperatures, developing sweet odours on the final parts.

Melt insensitive nucleants include a broad range of additives, among them the benzoate salts. Much used products are sodium benzoate and aluminium benzoate hydrates; another class of nucleants are sodium salts of organic phosphates; both families have melting or decomposition temperatures well above the normal processing temperatures used for PP and less effect in clarifying than the melt sensitive ones. The organic phosphates work as nucleant as well as clarifiers and, generally, we can say that all clarifiers do nucleation, but not all nucleant clarify well. Due to their melting point, very closed to the processing temperatures of PP, the melt sensitive nucleants are better dispersible in the PP matrix and more effective in their ability to improve both the thermo-mechanic properties and the clarity. The melt insensitive nucleants request a higher mixing energy to disperse themselves in the polymeric matrix. Some inorganic fillers may have effects on the morphology of the polymer crystals and on the kinetic of their formation. Due to their behaviour to the manufacturing temperatures, they may be considered as "melt insensitive" nucleants. A typical filler for this purpose is talc. A lot of trials were carried on some grades of talcs, different because of their micronization and the mineral source (structure and composition), comparing their nucleating effect with other typical nucleants. Nucleating agents are added in percentages from 0.01% up to a maximum of 1%, however in practice the percentages added are 0.2-0.5%.

| Type of nucleating agent | Chemical composition             |
|--------------------------|----------------------------------|
| Melt intensive           | Al Benzoate hydrate              |
| Melt intensive           | Na benzoate micronized           |
| Melt intensive           | Na salt of diterbutylbenzoate    |
| Melt sensitive           | 3,4 dimethylbenzylidene sorbitol |
| Melt intensive           | Mg silicate talc micronized      |

### Conclusion

The aim of this article:

Give small resume of what is a crystal, what is the what is a semi-crystalline polymer, what is the influence of nucleating agents on the crystallization process of polymers.

Give a non-exhaustive list of which are the commercial available nucleating agents.

For this work are be used images and examples found on various websites without that any of these sites was used as a reference. I hope that this work will be useful to all those who will read it.