Plastics Topics – Shrinkage in plastics processing

TANGRAM TECHNOLOGY | **Consulting Engineers**

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Contents

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1.   Introduction

The shrinkage of plastics after moulding causes diverse problems for processors and users. The phenomenon affects all plastics to varying degrees and the aim of this review is to give an overview of this effect to enable a common information base.

2.   Types of plastic

Most people are familiar with the conventional division of plastics into:

- Thermoplastics - can be remelted and reformed
- Thermosets - solidify and cannot be remelted
- Rubbers - a special case

In our case we are only interested in thermoplastics and these can be further sub-divided into:

Amorphous - these are plastics where the polymer chains have no well-defined order in either the solid or liquid states. Examples of such materials are PMMA (polymethylmethacrylate or Perspex), PS (Polystyrene), PVC and ABS. The structure is illustrated in Figure 1.

As a general rule any polymer which can be produced in a glass clear form is an amorphous type.
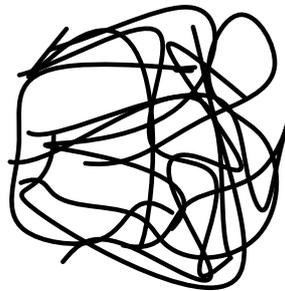
Figure 1: Amorphous polymer structure

Crystalline - these are plastics where a well-defined crystal structure forms. There are several models and theories for the crystal formation but the most popular involves a 'fringed micelle' model. This is shown in Figure 2 in the 2-dimensional form. This shows the ordered regions (crystallites) embedded in an amorphous matrix. Crystal formation begins at nucleation points and extends outwards into the bulk of the polymer.

Larger structures, composed of bundles of crystallites, are termed spherulites and these are formed in the bulk of the material. This is the same process as the formation and growth of grains in a metal.
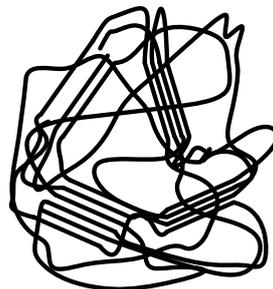
Figure 2: Semi-crystalline polymer structure

The important point with regard to any consideration of shrinkage is that the formation of crystallites gives better packing of the polymer chains and hence increased shrinkage.
Examples of crystalline polymers are PP (polypropylene), PE (polyethylene), PA (polyamide or nylon) and POM (polyoxymethylenes or acetals).

As a general rule crystalline polymers cannot be produced in a glass clear form.

Plastics Topics – Shrinkage in plastics processing

3. Types of shrinkage

Shrinkage is based on the compressibility and the thermal expansion of plastics. In crystalline plastics the phase transition in the crystalline portion of the material increases the shrinkage considerably.

Compressibility and temperature shrinkage

The compression and temperature effects on shrinkage are best discussed in terms of the moulding cycle as the major effect of these is actually seen within the cycle. The strict analysis of these requires consideration of the p-V-T diagram (Pressure-Volume-Temperature diagram) and a typical diagram for PS is shown in Figure 3.
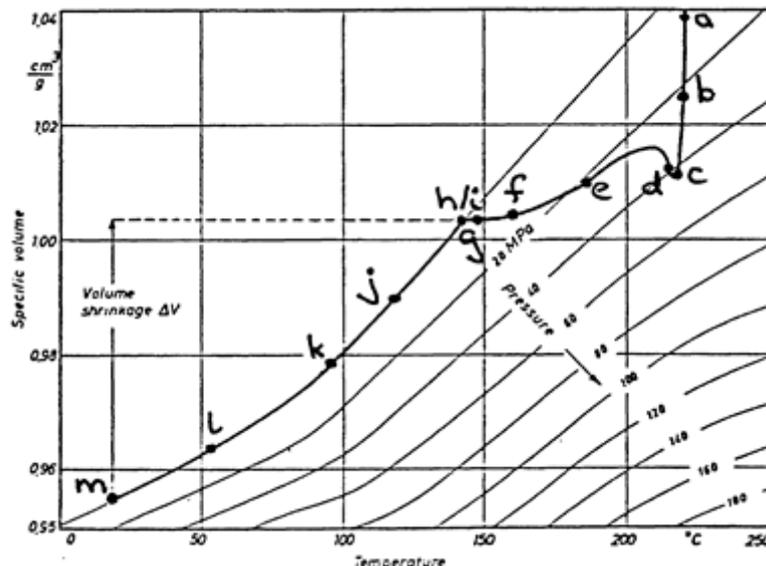

Figure 3: p-V-T diagram for PS

The process is:

1. The screw begins to advance and compresses the immediately in front of the tip. This forces the through the runner system to begin filling the cavity.
2. The cavity is filled.
3. The melt in the cavity is compressed until the maximum pressure is attained.
4. Switchover from injection to holding pressure.
5. Pressure drop from switching - more material from barrel.
6. Holding pressure attained but pressure drops due to volume contraction during cooling and decompression. Holding pressure pushes more melt into cavity and volume is maintained.
7. The gate is frozen and no more material is supplied.
8. Pressure drop from cooling, volume remains constant.
9. Atmospheric pressure reached, moulding separates from cavity wall to begin shrinkage.
10. Cooling at constant pressure.
11. Solidification.
12. Ejection.
13. Final state.

As marked on the p-V-T diagram above the volume shrinkage at this stage is almost totally defined by the co-efficient of thermal expansion and, to a lesser degree, the moulding parameters.

Examination of shrinkage values for amorphous polymers, where this is the only effect present shows that shrinkage values are not only low but also that the range of shrinkage is small for a given plastic. For a typical amorphous polymer, the shrinkage will be 0.3 - 0.7%. This is simply shrinkage due to cooling the polymer from about 150°C (the temperature of the melt at shut-off) to 23°C (room temperature) and can be related to the co-efficient of thermal expansion.

Plastics Topics – Shrinkage in plastics processing

Other factors, such as part geometry, orientation and moulding parameters have been ignored in this simple explanation but are considered later.

As a general rule the shrinkage of amorphous polymers is 90-95% complete at ejection and 100% complete within 3 to 4 hours. In any case the shrinkage is small enough that the 5-10% shrinkage which occurs post-ejection is not normally functionally effective.

It is generally true that the moulding tolerances achievable for amorphous polymers are far better than those achievable for crystalline polymers.

Shrinkage values parallel to and at right angles to the flow direction will also vary in amorphous polymers. Generally, shrinkage parallel to the flow direction is greater than at right angles to the flow direction. This effect is due to orientation and stretching of the molecules and subsequent relaxation. This effect is again far more pronounced for crystalline polymers where crystallisation shrinkage effects are also present.

Crystallisation Shrinkage

Crystalline polymers are affected by compressibility and temperature shrinkage and also by crystallisation shrinkage.

In the melt phase there is no order in crystalline polymers (their structure is similar to Figure 1), but as the polymer solidifies then the crystal structure forms (see Figure 2) and the more efficient packing of the polymer chains leads to significant volume shrinkage.

This is shown in Figure 4 for PP. The change in specific volume leads to shrinkage effects far greater than those seen in amorphous polymers.
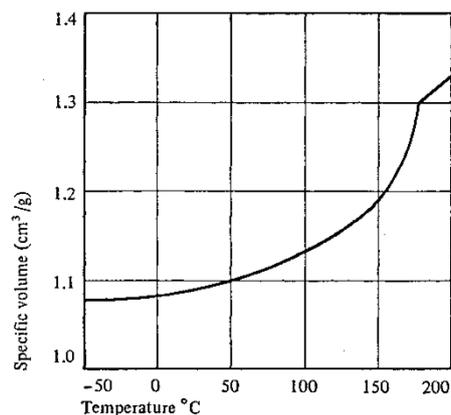
Figure 4: Specific volume of polypropylene vs temperature

The structure and properties of a given polymer will very much depend on the way crystallisation has taken place. A polymer mass with relatively few large crystals will be very different in properties to a polymer mass with far more, but smaller, crystals. There are two possible situations:

- 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.

- Heterogeneous nucleation - where particles in the polymer 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.

In either case the amount of crystallisation is dependent on temperature.

Before discussing the rate of crystallisation, we need to define two critical temperatures, these are:

- **Tg - The glass transition temperature:** Below Tg 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.

- **Tm - 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.

Plastics Topics – Shrinkage in plastics processing

The rate of crystallisation (both nucleation and growth) depends on temperature in a manner shown in Figure 5.
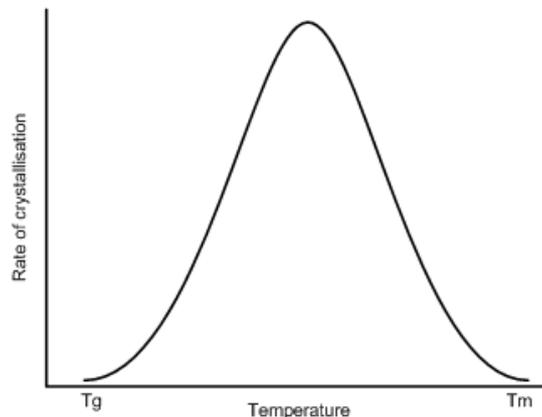
Figure 5: Typical form of crystallisation rate-temperature curve for a crystalline linear polymer.

The maximum rate of crystallisation occurs at a temperature of ½(Tm +Tg).

Above Tm no crystallisation exists (by definition of Tm) and below Tg no further movement of molecules is possible to nucleate or grow crystals. The fastest rate of crystallisation occurs midway between Tg and Tm. Hence the longer time that a polymer remains between Tg and Tm the greater will be the amount of crystallisation.

In many cases a warm mould (which reduces the cooling rate) will increase the amount of shrinkage.

- For PP the value of Tg is +5°C and Tm is 150°C. This means that PP will continue to crystallise slowly at room temperature (+21°C) until equilibrium is reached. 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. Raising the temperature speeds the process and in boiling water full shrinkage takes place within an hour.

- For polycarbonate (PC), Tg is +148°C and Tm is +250°C and no crystallisation can occur at room temperature.

- For POM, Tg is -13°C and Tm +160°C and hence the rate of crystallisation at room temperature is quite rapid and little measurable after-shrinkage occurs.

- For PA 66 a similar situation exists as for PP, i.e., Tg is only slightly less than room temperature and after-shrinkage can occur for up to two years after manufacture. In such cases it is normal to anneal the moulded article for a short time at the maximum crystallisation temperature to force the polymer to equilibrium.

Part Geometry and Section Thickness

Because polymers have a very low thermal conductivity, compared with metals, cooling from the melt proceeds unevenly, the surface cooling more rapidly than the interior. This leads to variations in the structure and crystallinity through the section thickness and can result in the formation of voids or holes due excessive internal shrinkage.

As a general rule thick sections take longer to cool and thus develop more shrinkage for all types of polymers.

The part geometry has an effect in two ways:

1. There is a difference in shrinkage parallel to and at right angles to the line of flow of the polymer. This is in fact associated not only with shrinkage but also with orientation. A reasonable allowance is to deduct 0.05 mm from the line of flow shrinkage figure.
2. Cooling will vary with distance from the gate. The melt temperature drops as the distance from the gate increases and the material sets at a faster rate. This can cause a difference in shrinkage between the inner and outer section and lead to warping.

Plastics Topics – Shrinkage in plastics processing

Mould cooling should be connected such that water is fed in first at the gate area and led to outer edge as it warms up. This will counteract the temperature gradient in the melt.

It is important to note that distortion of a moulding may not be solely due to shrinkage (of either amorphous or crystalline polymers) but may be due to high levels of moulded-in strain. High pressure and low temperature moulding can lead to low initial shrinkage but high levels of moulded in strain. Components can be tested for this by immersion in boiling water for 10 -15 minutes. If they are undistorted after this then they are unlikely to warp later.

4.   Reduction of shrinkage

Design (Part and Tool)

Product design to minimise shrinkage (and orientation/moulded-in stress) should conform to the conventional design rules for injection mouldings. The most critical of these are:

1.   Avoid any changes in cross section which can lead to differential shrinkage.
2.   Choose gate position to give linear flow across the moulding. If necessary, use multiple gates or a flash gate to give linear flow. This should avoid problems with differences between radial shrinkage and circumferential shrinkage.
3.   The gate must be a minimum of 0.75 mm and preferably 1.0 to 1.5 mm. The land length of the gate is also important and should not be greater than the diameter of the gate.

Process Variables - Amorphous Polymers

As noted above, shrinkage in amorphous polymers is mainly due to thermal expansion and shrinkage may be minimised by the following:

4.   Material feed temperature should be the minimum consistent with good flow and mouldings of satisfactory quality.
5.   Mould temperature should be the minimum consistent with mouldings of satisfactory quality.
6.   Packing time to be such that solidification at the gate has definitely occurred.
7.   Cooling time is such that a fully rigid 'skin' has formed on the moulding.

It is important to note that most of these factors will also reduce the total cycle time and give optimum production rates.

Process Variables - Crystalline Polymers

Most of the factors affecting amorphous polymers also affect crystalline polymers and the same remedies apply. In the case of crystalline polymers, a basic decision needs to be made. This is 'Do you force crystallisation and increase shrinkage at the moulding stage or not?'. For materials which do not continue to crystallise at room temperature crystallisation at the moulding stage should be minimised as it will not occur later. For materials such as PP, which continue to crystallise at room temperature shrinkage at the moulding stage should be maximised to reduce the amount of post-shrinkage that occurs and to allow assessment and acceptance of mouldings as soon as possible after moulding.

In order to maximise shrinkage during the moulding cycle the following rules should be followed:

1.   Increase mould temperature to force crystallisation almost to completion during moulding. Depending on the grade used and current setting it may be necessary to reduce the mould temperature to find the optimum point.
2.   Increase injection pressure to cause greater packing of the material and so counteract the volume reduction due to shrinkage.
3.   Increase injection time to allow more material to be packed into the mould.
4.   Reduce cylinder (melt) temperature. The ordered crystallite areas can provide sites for nucleation and reducing the melt temperature preserves these sites so that rapid crystallisation occurs. This will increase the 'along-flow' shrinkage but will decrease the shrinkage 'across the flow' due to the orientation of the nucleation sites during processing.
5.   Increase MFI of material to allow easier mould filling at lower melt temperatures.
6.   Increase gate size to give unrestricted flow into mould.

The above setting guide assumes that wall thicknesses remain relatively constant. If wall thicknesses vary greatly through the moulding, then the lower cooling rates in the centre of thick sections can lead

to varying degrees of crystallinity and hence shrinkage variations from point to point. This uneven shrinkage also sets up stresses which can lead to distortion.

A large factor in distortion and shrinkage is an excessive difference in the 'along-flow' and 'across-flow' shrinkages. If the difference is excessive and distortion is a problem the following checks should be made:

1. Decrease injection pressure and raise cylinder (melt) temperature.
2. Check mould temperature and cooling feed.
3. Increase number of gates.

Material Variables - Crystalline Polymers

High nucleation and growth rates can be achieved if heterogeneous nucleation is used. In this case, nucleation is initiated by seeding with a foreign particle, frequently this is a polymer similar to the base polymer but with a higher melting point. Some commercial products incorporate nucleating agents to give rapid freezing, a high degree of crystallisation and controlled structures. In some cases, the presence of a colourant can act as a nucleation agent and create different crystallisation and shrinkage for different colours!

5.   Measurement of shrinkage

Shrinkage is expressed either as a percentage or as a ratio (mm/mm) and the values obtained for a particular grade of material are dependent on processing conditions and mould design.

Formulae

A component is moulded from a cavity of known dimensions (at 23^oC) and allowed to cool to 23^oC. Measurements are made after a specified time.

- Mould Shrinkage (%) = $\dfrac{L_0 - L_1}{L_0}$ x 100

  L_0 = Length in mm of cavity

  L_1 = Length in mm of component

- Post-moulding shrinkage (%) = $\dfrac{L_1 - L_2}{L_1}$ x 100

  L_1 = Length in mm of component (original)

  L_2 = Length in mm of component after a given time (24 hours, 48 hours or 168 hours) at a certain heat treatment.

Test Methods

In the most common tests, a special test bar is moulded (3 times) and the dimensions measured at 1-2 hours (for samples 3.2mm thick) and again at 24 and 48 hours.
The values produced by these methods are only guidelines as practical shrinkage is dependent on many factors.