aptiv™

VICTREX® PEEK™ FILM TECHNOLOGY

Thermoforming APTIV™ Film

About this guide

This guide is provided to our customers as a reference tool for the thermoforming process. The following notes may be applied to any of the commonly used forming techniques. There are no exact rules that can be given for thermoforming APTIV film. Many variables such as part design, process equipment and film thickness will influence the process.

It is assumed for the majority of this guide amorphous APTIV film is being used as the starting material for the thermoforming process. Section 2 is relevant for shaping crystalline APTIV film. It is normally expected that the final thermoformed part will be crystalline in nature to obtain the best properties of PEEK in the final application. Shaping of PEEK polymer can be achieved with 3 methods outlined in this document, but the method is highly dependant upon the starting form of PEEK (amorphous or crystalline), the process temperatures used and thickness required in the finished part.

Introduction to VICTREX® PEEK™ Polymer

VICTREX® PEEK™ polymer is a high-temperature, semi-crystalline thermoplastic which provides a unique combination of properties to Engineers, Designers & OEM's. As a thermoplastic polymer PEEK can be extruded or injection moulded into a variety of shapes and forms, one important form is cast film. A graph of modulus against temperature for typical amorphous & crystalline polymers is shown in figure 1 to illustrate some key points to be understood as part of this guide.

Thin films of PEEK can be made amorphous due to the method of manufacturing the film. This amorphous film is optically clear in nature with a light brown colour. This amorphous APTIV film can be thermoformed at temperatures of 140-160 °C (284-320 °F) using common forming techniques such as vacuum forming, drape forming, air slip forming and plug assist forming. The thermoforming technique used will depend upon both the dimensions of the article to be formed and its tolerance specification.

Amorphous APTIV film is typically available in thickness from 25 μm to 250 μm (1 to 10 mils).

PEEK polymer has a glass transition temperature (T_g) of 143 °C (289 °F) and a crystalline melting point (Tm) of 343 °C (649 °F). Amorphous APTIV film can be annealed by heating it to temperatures above its T_g to induce crystallinity, thus enhancing both heat stability and chemical resistance.

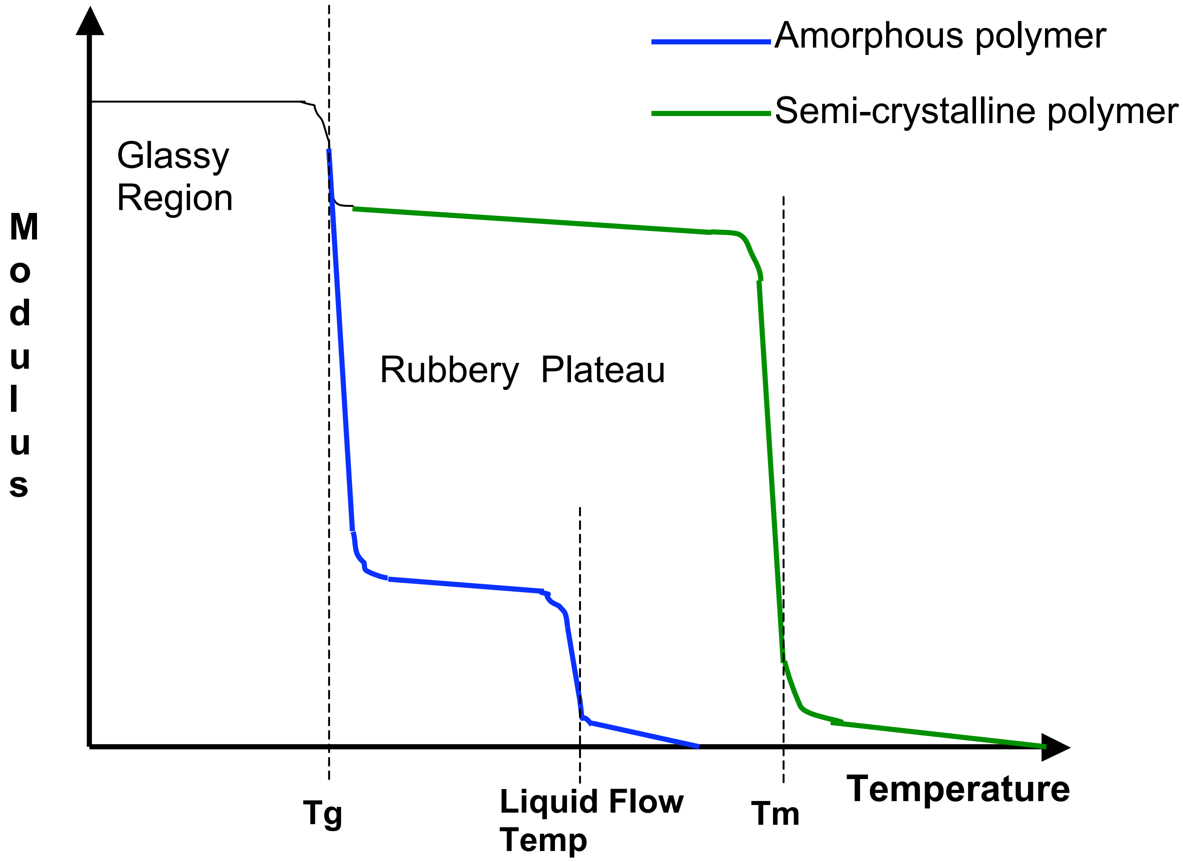


Figure 1 – Schematic of temperature dependant modulus for amorphous & semi-crystalline polymers

PEEK^{TM} Polymer Crystallinity

It is vital that the processors understand the crystalline nature of PEEK polymer which is very important to successful thermoforming of the product. The amorphous film is optically clear in nature with a light brown colour, where as the crystalline film is a light tan colour & optically opaque. PEEK behaves as a crystallising polymer when thermoforming from amorphous film above the glass transition temperature (Tg) – see Section 3.

The lowest energy state of PEEK polymer is in the semi-crystalline form & PEEK will always try to reach that lowest energy semi-crystalline state if the molecules are sufficiently thermally mobile to re-order themselves. This happens at temperatures above the Tg of 143 °C. Once above the glass transition temp of 143 °C, amorphous PEEK will rapidly begin to revert into the crystalline state in the order of 2-20 seconds and the crystallisation process can have completed in as little as 10-30 seconds depending upon the temperature (see Fig 2). This crystallising behaviour of amorphous PEEK above Tg is considered exceptional amongst most of the polymers commercially available today and may be unfamiliar to some of the processors trying to thermoform PEEK parts.

The tensile modulus of the amorphous film & the crystalline film differ significantly with the crystalline form being approx 40% higher than the amorphous form. Given this difference in modulus it is easier to shape the amorphous form of the polymer. However upon heating to 160 °C there is a small process window where the amorphous phase has sufficiently softened to allow easy drawing of the polymer without reversion to crystalline form having taken place. If you attempt to shape the crystalline form of PEEK then you will need to take the material to much closer to the melting temperature around 300-340 °C to effectively shape crystalline APTIV film - see section 2.

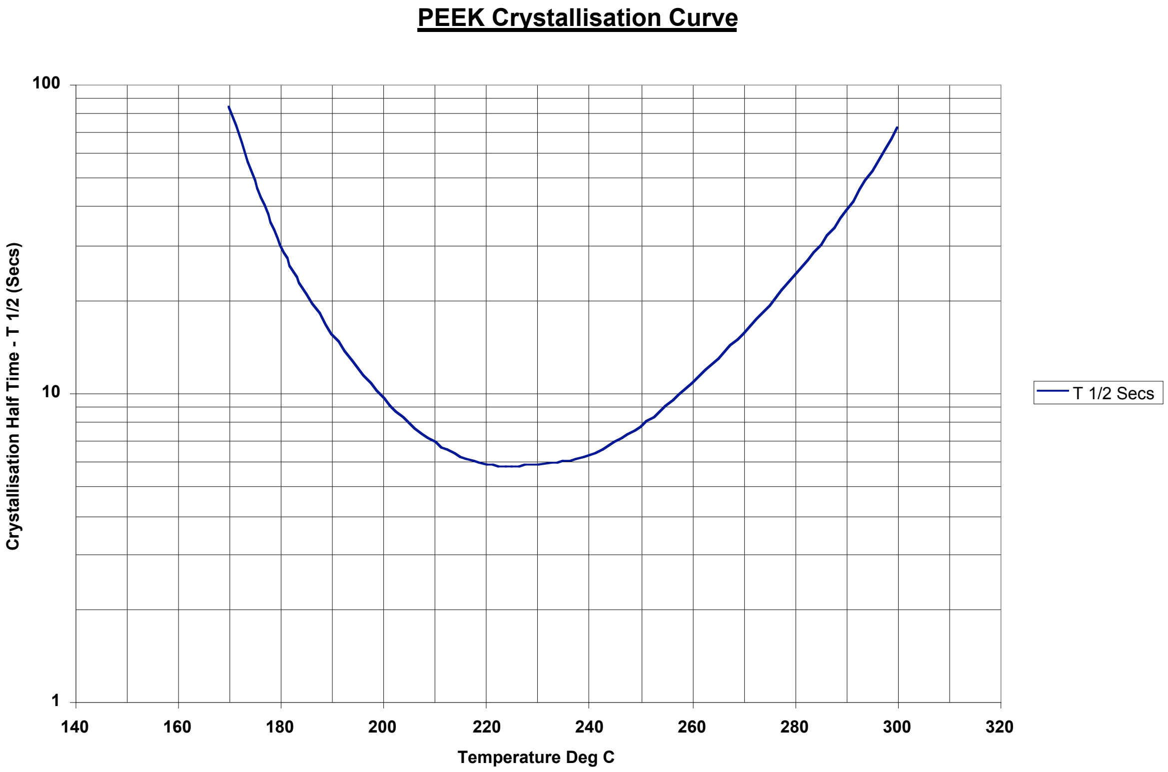


Figure 2 – PEEK Crystallisation half-time curve

Process Control

The most important factor when using **ANY** of the forming methods for APTIV film is the accurate control of the both the mould temperature and the temperature of the polymer. The reader will see from this guide that the different process temperatures will have a dramatic effect on their ability to accurately & reproducibly thermoform parts from APTIV film. Many processors rely primarily upon time as the key process parameter, but as the forming temperature of PEEK is critical, it is possible that this control method may not yield sufficient consistency in the process and the resulting parts.

Time is still an important factor, particularly when using the methods in Section 3, where the APTIV film is changing from an amorphous material to a crystalline material during the shaping process. The combination of **temperature and time** must both be controlled in this type of process to achieve consistent results.

We highly recommend that the mould tools have a thermocouple capability to measure the temperature of the process, and that timers are used for each stage of the forming process. If the thermoforming machine is not fitted with a pyrometer to monitor sheet temperature, then the optimum forming point of APTIV film is easily observed visually. As heat is applied to an amorphous film, a relaxation in the film is first seen as the temperature reaches Tg 143 °C (289 °F); this is shortly followed by the whole area of the film becoming taut. As soon as the film is taut, forming must take place; further heating will only cause the film to crystallise. (see Section 3).

Sandwich heaters are not required because the material is relatively thin. The heater depositing range on a single (top or bottom) heater bank should be the order of 0.17 to 0.26 KW/m^2 (1.86 to 2.8 KW/ft^2). Again, care must be taken to balance the heaters correctly if they have variable intensity control. Hot spots may cause areas of film to crystallise which will in turn lead to forming problems.

Drying & Preparation of the Film

The film should not require drying prior to thermoforming as PEEK has a very low moisture absorption level. If blistering does occur the film can be dried at temperatures of up to 130 °C for 2-4 hours depending upon sheet thickness. Care should be taken to remove any dust or grease from the film. PEEK is resistant to most common degreasing agents.

Moulds / Tools

Amorphous APTIV film can be formed on a cold tool which must be below Tg. Typical tool temperatures for cold forming would be <130 °C (266 °F). This will maintain the film's amorphous properties such as optical clarity, low haze and heat seal-ability. (Section 1)

Crystalline APTIV film may also be formed onto a hot tool approaching Tm, (300-340 °C). This method will maintain the crystalline nature of the polymer giving improved rigidity at high temperatures, with better wear and chemical resistance. (Section 2)

Amorphous APTIV film may also be formed onto a hot tool above Tg, (140-170 °C) to crystallise the film and give improved rigidity at high temperatures and better chemical resistance, but with the loss of optical clarity. (Section 3)

Materials of construction for Tools

Cheap tools made from wood or cast epoxy resin may be used as prototypes or for small production runs. These will be particularly cost effective when using the cold process in section 1. Aluminium, stainless steel or mild steel should be used to manufacture heated tools and for longer runs, where accurate heating distribution and dimensional tolerances are required.

Mould Removal

APTIV film may easily be ejected from the forming tool using an air blast. Heating of metal forming tools between 100 and 130 °C (212 and 266 °F) will assist release. When forming APTIV film, followed by crystallisation on the tool, cooling of the tool to 130 °C (266 °F) may be required to increase the rigidity of the film for mould release. It is preferable that the polymer is below Tg (143 °C) for the mould removal process to prevent any further deformation of the part. If a fully crystalline part is being made then release temperatures above Tg can be used as the modulus of the part is still relatively high.

Part Trimming

The thermoformed part can be trimmed by a variety of methods to produce the final finished part. Examples of such trimming methods include steel rule dies, routers, saws through to water jets & laser cutting devices.

Section 1: Thermoforming Amorphous Polymers

Amorphous polymers, such as Polycarbonate (PC), Polyethersulphone (PES) & Polyether-imide (PEI), do not crystallise due to their chemical structure and are normally optically clear. Amorphous polymers are used in service below their Tg but need to be taken above their Tg to be thermoformed. Taking amorphous polymers above Tg will cause a significant drop in the modulus of the polymer making the shaping of the polymer much easier. Once the part has been shaped at this elevated temperature the part is usually cooled back below Tg to allow removal of the part from the mould. As there are no changes in crystallinity with amorphous polymers, the forming process is relatively straight forward.
Most thermoformers will be familiar with this class of polymers.

PEEK can be thermoformed as an amorphous polymer if all the process temperatures throughout the operation are kept at a safe margin below Tg of 143 °C (289 °F). We suggest this would be done up to temperatures of 130°C maximum.

Amorphous APTIV film can only be manufactured to a maximum thickness of approx 250 microns. This is due to the fast quenching rate required to prevent the crystallisation of the polymer directly from the melt. This section is therefore relevant for part designs up to 250 microns in thickness.

IF THE TEMPERATURE EXCEEDS 140°C (Tg) THEN PROCESSORS SHOULD USE THE DETAILS IN SECTION 3 (Thermoforming Crystallising Polymers).

Forming onto a “Cold” Tool

Tool temperatures of up to 130 °C (266 °F) may be used to form amorphous APTIV film. The film may also be pre-heated to a maximum of 130°C to lower the modulus & allow easier shaping. At 130 °C (266 °F), heat loss from the film is minimised to allow maximum drawdown and mould definition before freezing.
The film still remains rigid enough to allow easy ejection by air blast and will not crystallise. Tool temperatures between 100 °C (212 °F) and 130 °C (266 °F) may also ease removal of the part when using metal tooling.

Section 2: Thermoforming Semi-Crystalline Polymers

Semi-crystalline polymers such as both low & high density polyethylene (LDPE & HDPE), Polypropylene (PP) & Polyamides (Nylons) will form order & structured domains on cooling from the melt. Semi-crystalline polymers are typical opaque in nature as the crystallites cause diffraction of the light making the polymer appear opaque. The structured domains are typically referred to as crystallites in polymer terms, though the term spherulites can also be used to describe the polymer crystals. Regions of the polymer are still amorphous with crystal structures in amongst the amorphous domains. As in the fully amorphous case, taking the polymer above the Tg will allow the amorphous regions to soften causing a slight drop in the modulus. However at temperatures above Tg & below Tm the crystallites do not melt & provide most of the modulus for the polymer in the so called rubbery region. Only when the film is taken very close to the melt point (Tm) do the crystallites melt & the modulus drops off significantly. The thermoforming of semi-crystalline parts is typically done at a higher temperature much closer to the melt temperature of the polymer. The polymer film is taken closer to the melt temperature to get the crystals in the polymer to melt, allowing easy shaping of the part.

PEEK can be formed as a crystalline polymer but this method needs to be used with a typical process temp of 300-340 Deg C. The high temperature allows the polymer crystals to melt and lowering the modulus to allow shaping to take place. See the DMTA graph modulus vs. temperature in Figure 3.

Processors will need to check the temperature capability of their equipment as temperatures of 300-340C is typically much higher than the capability of normal thermoforming equipment.

Crystalline APTIV film can be made in a broad range of thicknesses from 25 microns to in excess of 1000 microns. This section will be particularly relevant for thicker section parts (typically >100microns) where crystalline parts are required as the final form.

Section 3: Thermoforming Crystallising Polymers

This is a actually a combination of the above two cases where the polymer starts out as an amorphous film, but as a result of the heating above Tg to form the part, it will end up as a semi-crystalline material by the end of the process. Probably the most typical example of this is crystallisable polyethylene terephthalate (CPET), but more importantly PEEK polymer also falls into this category.

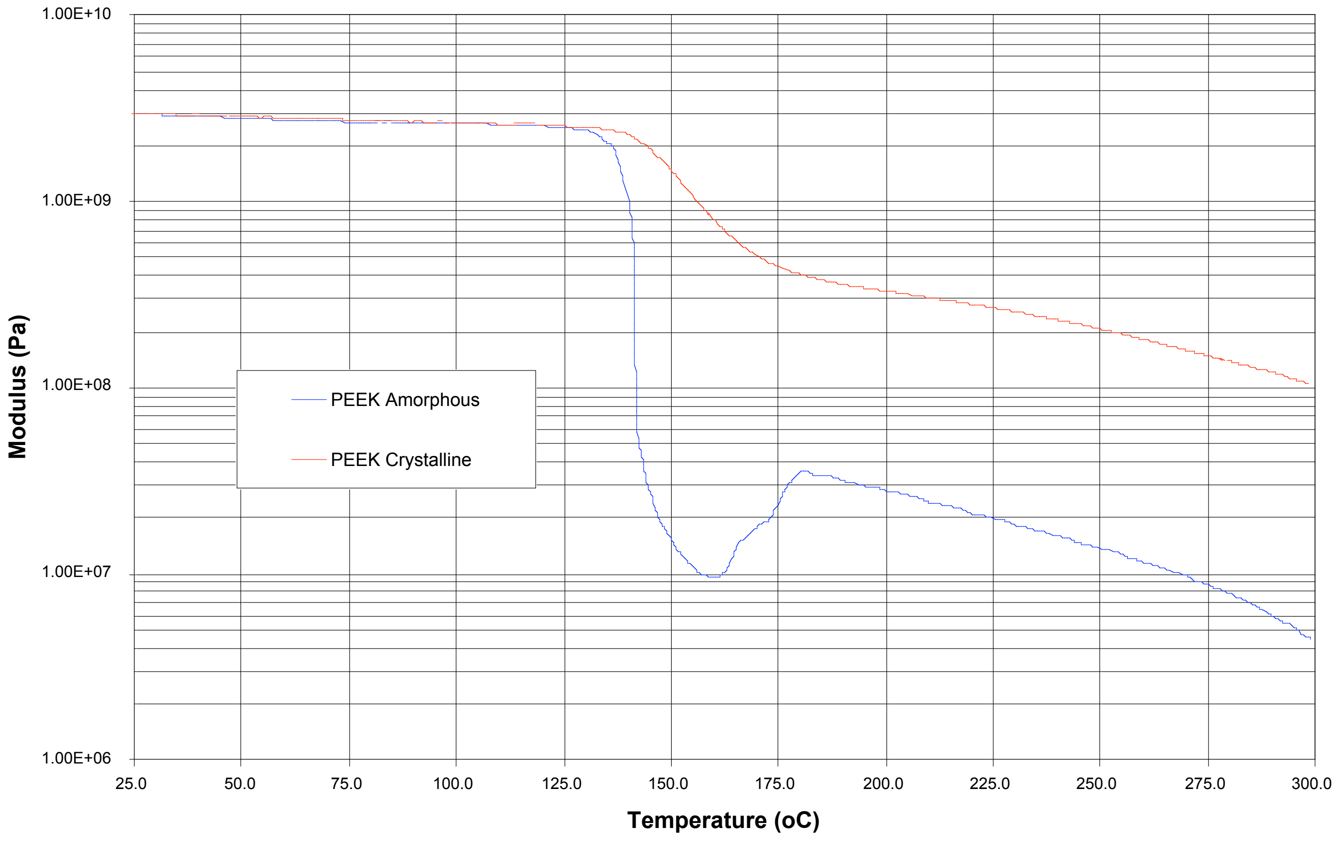
This crystallising behaviour is considered as exceptional in the polymer world where the majority of polymers do not change their crystalline state over a thermal cycle. Processors may not have come across such a class of polymers before & need to understand this crystallising behaviour to be able to arrive at a suitable set of process conditions to produce an acceptable thermoformed part. The rate of crystallisation in these polymers is dependant upon temperature (see fig 2) and so a dynamic system is created where the modulus is decreasing with the increase in temperature, and at the same time the modulus is increasing as the crystal structures develop at a rate dependant upon the temperature. Which of these factors dominates the modulus makes precise prediction of thermoforming conditions of this class of polymers much harder to provide precise guidelines. Factors such as film thickness, residence time, heating rates & draw ratio of the part will all have a bearing upon the process.

For this class of polymers the heating time should be as short as possible so that modulus reduction occurs without developing any of the crystallites, and the formability of the material remains good. Higher levels of crystallinity developed in the film before forming, caused by long heating times, will prevent good part definition. Once the part has been formed a hold period should be incorporated in the cycle to allow the crystalline structure to fully develop in the polymer. This will prevent dimensional changes due to further crystallisation on any subsequent heating cycle.

A DMTA graph of the amorphous PEEK is shown below (Figure 3), run at a constant heating rate and taken above the Tg. It shows that the film will soften for a short period before the crystallisation effects cause an increase in the modulus.

Amorphous APTIV film can only be manufactured to a maximum thickness of approx 250 microns. This is due to the fast quenching rate required to prevent the crystallisation of the polymer directly from the melt. This section is therefore relevant for part designs up to 250 microns in thickness.

Figure 3 – DMTA graph of modulus against temperature for Amorphous PEEK polymer taken above Tg, with crystalline film shown for reference purposes.



Heating the APTIV™ Film

Amorphous APTIV film will gradually lose modulus as it is heated and will begin to soften more significantly at temperatures above 143 °C (289 °F). However, because PEEK is an inherently crystalline polymer, it will quickly start to crystallise at temperatures above its Tg at 143 °C. If crystallisation is allowed to take place, then the film will become too rigid to easily thermoform at temperatures around 140-160 °C (284-320°F). Heating times should be started as short as possible and only increased gradually until the shaping process becomes difficult indicating that crystallisation has occurred.

It is essential **not** to allow the film to crystallise before shaping, so we recommend using forming temperatures in the range of 140-160 °C (284-320 °F). It is important to note that when the film crystallises, it becomes opaque. The film forming temperature should be reached as rapidly as possible to minimise the cycle time and also reduce the possibility of film crystallisation.

The thickness of the film has an important effect on the heating rate, and therefore the crystallisation rate. When using thinner films of less than 50 microns, temperatures of 150°C or slightly lower are recommended so that crystallisation doesn't occur before stretching. We would recommend that for the thin films, processors start with a forming temperature of 140C & gradually increase temps from there to accurately determine their optimum heating temperature. For films above 50 microns then the 160°C forming temperature is probably more appropriate with crystallisation not occurring as fast.

Forming Times

The time between the APTIV film reaching its optimum forming temperature and the forming taking place must be kept to a minimum, typically <20 seconds. In the case of very thin films of around 25 microns, this time can be as little as 5 seconds to reach forming temperature. If the pre-heat time is too long then crystallisation will begin to occur and affect the ability of the film to be formed. The short times will allow maximum draw ratios and good mould definition to be obtained. If using drape forming or air slip forming, vacuum assist is recommended to ensure good mould definition and reproducibility.

It is also possible to induce a level of crystallisation in the stretched sections of the part from the process of strain induced crystallisation. The normal method of crystallisation is from thermal energy. This strain induced crystallisation can occur when the amorphous material is above Tg & the molecules can re-order themselves. As the section is stretched out, the molecules will re-order themselves in to crystalline sections from the alignment of the molecules achieved during the stretching. If sections of thin films are drawn to a high ratio, then such crystallisation maybe observed by the need for increasing draw force as the part is stretched.

A period of time needs to be built in the process once the material has been correctly shaped with the mould temperature above Tg. This will allow the crystallinity of the PEEK film to fully develop. If the part is removed before complete crystallisation has taken place them any subsequent heating above Tg may cause final stage of crystallisation to occur which will affect the part accuracy & dimensions. Optimum temperatures for crystallisation will depend upon required cycle times and the shape to be formed, but will be in the range of 160-220 °C (320-428 °F). There is no advantage in heating the tool to temperatures in excess of 220 °C (428 °F) - this will not increase crystallisation rates (see fig 2).

It is important that the polymer is below or very close to Tg (143 °C) for the mould removal process to prevent any further deformation of the part. PEEK film may easily be ejected from the forming tool using an air blast. When forming APTIV film, followed by crystallisation on the tool, cooling of the tool to 130 °C (266 °F) may be required to increase the rigidity of the film for mould release.

Post Forming Annealing

It is possible that parts made by the method in section 3 may be annealed after the part has been removed from the mould. The purpose of this process will be to relieve any stresses which may have been induced in the part during the forming process. This process will be conducted as a temperature cycle of heating and cooling in an air circulating oven. The temperatures should be taken to a maximum of 260 °C (500 °F) and cooled to around Tg 143 °C before removing from the oven.

It should be noted that if the part has not sufficiently crystallised during the forming process, dimensional changes in the part may occur upon this subsequent heating. This post process annealing step should be conducted as part of the process development for the parts to determine that the part has reached satisfactory dimensional stability. If the part is to be subjected to operating temperatures at the same level or above the maximum process temperature during the forming process, we recommend that processors conduct this as a quality check for functionality of the part design.

If the part is seen to change dimensions during such a post forming annealing, then the process should be modified to increase the crystallinity of the parts during the process. This can be achieved by either a longer holding time after forming, or going to a higher temperature during the holding stage. This can also be checked by conducting a crystallinity measurement by DSC on the part after forming and after an annealing process. Significant increases in the levels of crystallinity due to a post forming annealing step would indicate a potential issue with the process not achieving full crystallinity in the part.

About Victrex

Victrex plc is the leading manufacturer of high performance materials, including VICTREX® PEEK™ polymer, VICOTE® Coatings and APTIV™ film. These materials are used in a variety of markets and offer an exceptional combination of properties to help processors and end users reach new levels of cost savings, quality, and performance.

The company is headquartered in the UK. Invibio®, Victrex's biomaterials business, provides access to specialized products and services for medical device manufacturers. Victrex Japan, Inc. is a wholly-owned subsidiary of Victrex plc. For more information visit http://www.victrex.com or www.victrex.mobi.

For more information about Victrex APTIV™ films made from VICTREX® PEEK™ polymer, go to www.aptivfilms.com.