

THERMOPLASTIC MATERIALS

Introduction to Thermoplastic Materials

Plastics are a group of materials made up of long molecules, often referred to in scientific terms as macromolecules or more commonly as polymers (translated from Greek as meaning 'many units').

Polymers are formed by joining together many small simple molecules, called monomers, into a long chain. By starting with different monomers it is possible to build up a large series of polymers with wide ranging properties. The process by which monomer molecules are joined is known as polymerisation.

Plastics materials can be divided into two main categories: thermosets and thermoplastics. Thermosets are materials that on heating form a three-dimensional, cross-linked network of polymer molecules. The formation of a cross-linked structure is irreversible and thermosets as a result cannot be softened again without decomposition occurring.

Thermoplastics are characterised by their ability to be repeatedly softened at elevated temperatures and solidified by cooling. Due to the molecular structure of these materials, they do not undergo any chemical change during thermoforming so the heating and forming cycle may be repeated several times.



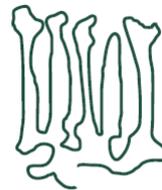
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Thermoplastics represent the most important class of plastics materials commercially available. They are more difficult to categorise owing to the wide variety of different polymers whose properties can vary quite considerably from one another. However, within this class of materials there are two main groups that assist in clarifying properties:

- Crystalline polymers;
- Amorphous polymers.



Amorphous



Semi-Crystalline

Polymer chain configuration for amorphous and semi-crystalline polymer

Crystalline polymers tend to be tougher, softer and translucent to opaque with higher heat resistance and density compared to amorphous thermoplastics. They show a greater resistance to fatigue, wear, abrasion and chemicals. Shrinkage levels are much higher giving poorer control over dimensional stability. As the name suggests these materials have crystalline or ordered regions, the magnitude of which greatly affects their properties.

Examples of crystalline thermoplastics include: polyethylene (PE), polypropylene (PP), nylon (PA – polyamides) and polyethylene terephthalate (PET).

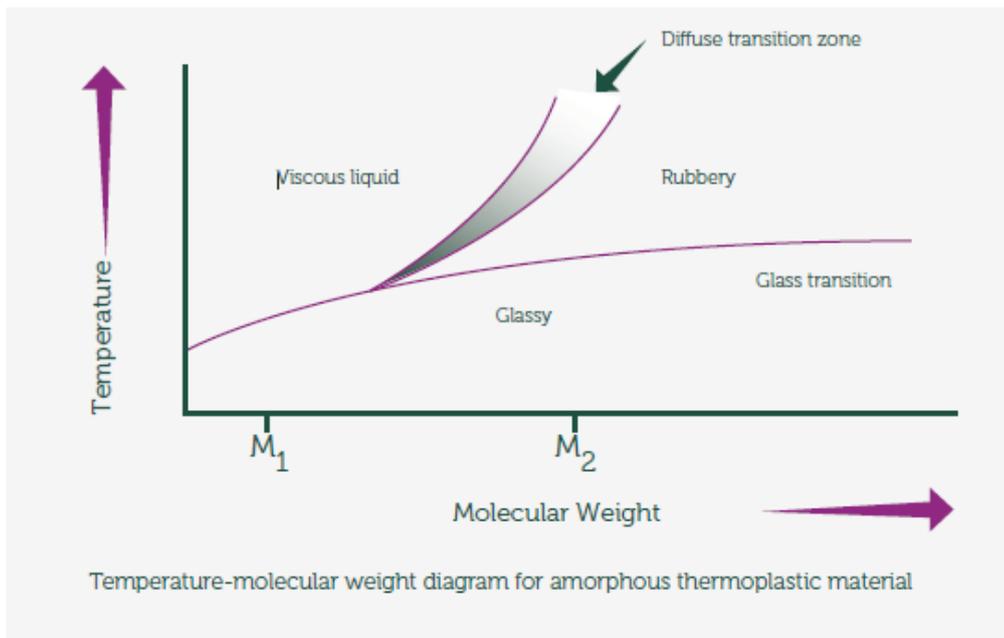
Amorphous polymers are typically hard, clear, high-gloss, rigid materials with low shrinkage (good dimensional control). Typically the toughness of such materials can be enhanced, particularly with respect to impact strength, by incorporating a rubber additive. These are exemplified by materials such as high-impact polystyrene and ABS.

Examples of amorphous thermoplastics include: polymethyl methacrylate (PMMA), polystyrene (PS), high-impact polystyrene (HIPS), acrylonitrile-butadiene-styrene (ABS) and poly vinyl chloride (PVC).

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Thermoforming Characteristics of Thermoplastics

With amorphous polymers there is no clearly defined melting point from a solid phase to a liquid on heating - there is instead a rubbery intermediate zone.



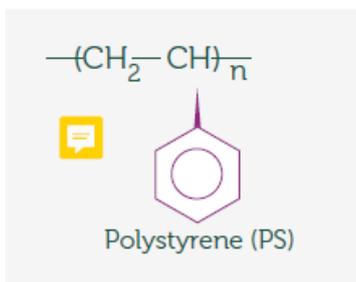
If a rigid sheet of thermoplastic material is heated at some point, as the temperature rises, it will become flexible or rubbery. This is the transition point at which it enters the thermoforming range and successful forming requires working in this range. What is of importance is the temperature range within which the sheet becomes rubbery - this can vary from polymer to polymer. Obviously if this range is narrow it is important to have very close control of the operation. It is desirable for a good thermoforming material to become soft and rubbery over a wide range, rather than have a sharp melting point. In general amorphous materials (e.g. impact-modified polystyrene or ABS) exhibit wider thermoforming ranges than crystalline materials (e.g. polypropylene).

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Another important consideration in thermoforming is the condition of a material as it enters the rubbery stage - it can exhibit either elastic or plastic behaviour, or a combination of both. Essentially the elastic condition is a stage where the material is strong and elastic – in such a state the material exhibits good hot strength and can be stretched by as much as 500 to 600% (also referred to as high hot-tear-strength materials). In contrast are those materials that are predominantly plastic in nature – on heating they lose all their strength and become soft and putty-like. These materials have low hot elongations and may only stretch by 15 to 20% before tearing (i.e. low hot-strength materials). Over the usable thermoforming range of a material, both elastic and plastic properties may be identifiable, which may be dominated by one or other of these two states. Materials with a dominant elastic range are suitable for pressure or drape forming – if a material exhibits predominantly plastic behaviour in the thermoforming range then it is suitable for vacuum forming and high definition can be achieved.

Principle Thermoforming Materials

Polystyrene (PS), or as it is sometimes referred, crystal polystyrene (crystal PS), is a hard, rigid, transparent thermoplastic.



It has low moisture absorption, exhibits good dimensional stability and its natural base colour allows for a wide range of colouring. The optical properties of crystal PS are of importance as it has a high transmission of all wavelengths of visible light and its high refractive index gives it a particularly high `brilliance`. Because of its poor ultra-violet (UV) resistance it is not normally suited for outdoor use.

Crystal PS is generally not used in thermoforming - typical applications for sheet product are for textured shower panels. It is frequently used as a capping layer on impact-modified polystyrene sheet to impart a high gloss finish.

Identifying Crystal PS

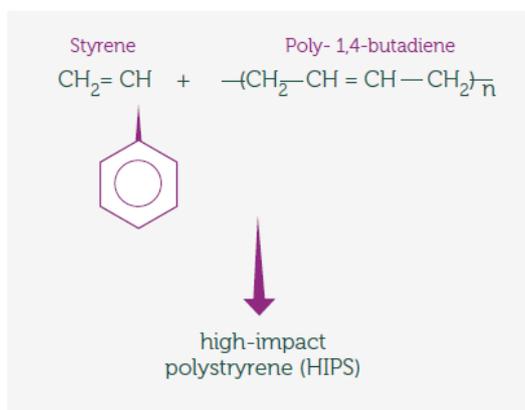
Crystal PS can be identified as follows:

- Density: does not float on water.
- Flame test: ignites readily; continues burning after removal of flame; drip burns with sooty flame – black smuts given off.
- Colour: transparent in natural form (unpigmented).

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Impact-Modified Polystyrene (HIPS)

For many applications crystal PS is considered to be too brittle a polymer. Because of this it can be modified by addition of rubbery additives, typically butadiene rubber.



Such impact-modified polystyrenes, depending on the amount of rubber added, can be classified as either medium or high-impact materials. A high-impact polystyrene (HIPS) may have six times the impact strength of crystal PS but about half the tensile strength and a lower hardness. Because of the rubber content there may be a reduction in light and heat stability. Obviously with the addition of rubber additives there is a loss in clarity. Typically impact-modified polystyrenes are translucent, though high-impact materials with a high degree of transparency are available.

Impact-modified polystyrenes are one of the most tolerant and forgiving materials to thermoform owing to the low thermoforming temperatures required and the almost immediate transition into the plastic state. Moisture absorption is generally not a problem and pre-drying is rarely required.

Identifying Impact-Modified Polystyrene

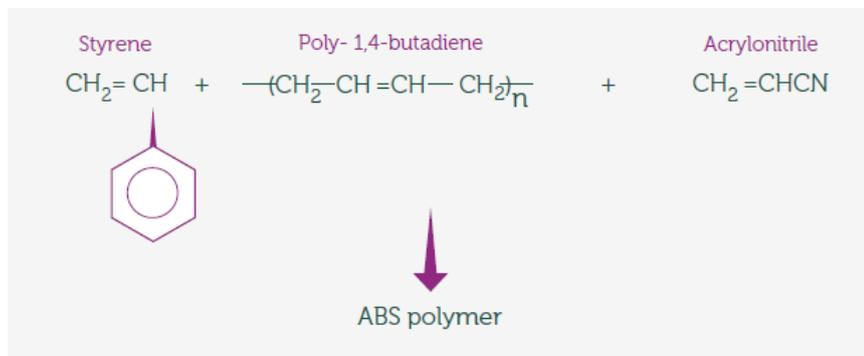
Impact-modified polystyrenes can be identified as follows:

- Density: does not float on water.
- Flame test: ignites readily producing yellow, sooty flame – black smuts given off; continues to burn after removal of flame; smells of rubber.
- Solvent test: wiping surface with 1,1,1-trichloroethane will cause softening of same (used to distinguish between HIPS and ABS polymers).

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Acrylonitrile-butadiene-styrene (ABS)

Acrylonitrile-butadiene-styrene (ABS) materials were developed to improve the impact strength and chemical resistance of the impact-modified polystyrenes. As the name suggests they are produced by polymerising butadiene rubber with acrylonitrile and styrene, and the possible combinations are such that a very large range of ABS-type polymers is commercially available.



ABS polymers have impact strengths up to 4 to 5 times that of high-impact polystyrene (HIPS) polymers and softening points as high and sometimes higher, than crystal polystyrene. Special flame retardant ABS grades are available by incorporation of fire retardant additives – apart from the expense of such additives there is also some loss in toughness associated with their use.

Similar to the impact-polystyrenes, ABS materials have a fairly wide melting range and as such are easily thermoformed. Owing to their higher softening points though, longer heating times are required. Within the thermoforming window ABS exhibits 50:50 plastic / elastic behaviour. Their heat stability is not as good as that of the polystyrenes and if temperatures are allowed to reach above 230°C noxious vapours are given off.

As ABS is a hygroscopic material pre-drying may be necessary as moisture absorption can be as high as 0.3% and, if present, will cause blisters to form when heated above 130°C.

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Identifying ABS

ABS polymers can be identified as follows:

- Density: does not float on water.
- Flame test: burns and does not drip; produces black smuts and smells of rubber.
- Solvent test: wiping surface with 1,1,1-trichloroethane will not affect same. This simple test can be used to distinguish between HIPS and ABS polymers.

Like most polymers, ABS has poor resistance to the effects of weathering, particularly exposure to sunlight, where ultra-violet (UV) light will attack the polymer resulting in embrittlement, discolouration and dulling effects. However, ABS sheet products can be protected from the harmful effects of UV radiation by incorporating a pigmented UV resistant polymer material as a co-extruded capping layer. There are two polymers of choice in this respect, both of which offer outstanding UV resistance:

- PMMA (polymethyl methacrylate, or acrylic polymer)
- ASA (acrylate-styrene-acrylonitrile polymer)

PMMA polymers provide superior UV resistance while offering a high gloss, high scratch resistant surface (matt grades are also available). In comparison ASA polymers offer excellent UV resistance combined with superior mechanical properties and chemical resistance.

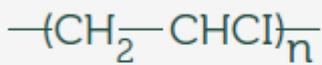
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Polyvinyl chloride (PVC)

Polyvinyl chloride (PVC) is a rigid and hard material that is quite brittle in its unplasticised form. By incorporating plasticizers and impact modifiers the toughness of PVC can be enhanced, i.e. it becomes a more flexible material. PVC exhibits excellent chemical resistance and is inherently self-extinguishing.

However, the chief drawbacks of PVC are its limited heat stability (does not lend itself to repeated reprocessing), high density (1.4 g/cm³ – poor weight / volume ratio), and limited availability (with respect to colour and gauge). The difficulties in recycling are important from an environmental viewpoint. In addition there can be problems with corrosive hydrogen chloride gas given off on incineration.

In terms of thermoforming characteristics PVC has a narrower processing “window” than materials such as HIPS and ABS – additionally definition of parts is poorer with PVC, particularly where sheet gauge in the range of 3.0 to 6.0mm (it is difficult to draw material into the final corners of the mould).



Polyvinyl chloride (PVC)

Identifying Polyvinyl chloride

PVC can be identified as follows:

- Density: does not float on water.
- Flame test: difficult to ignite; burns but is self-extinguishing on removal of flame source; flame colour has a touch of green.
Acrid smell produced.

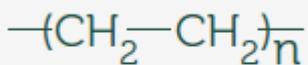
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Polyethylene (PE)

Polyethylene (PE) represents a group of materials that are tough waxy solids, with a slightly translucent appearance, and are semi-crystalline in nature.

Polyethylene polymers can be classified according to density - either low density or high density (LDPE and HDPE respectively), the different densities reflecting the different types of molecular configuration and crystallinity. The greater the density the higher the softening point, rigidity and surface hardness. For both materials water absorption is negligible and they are resistant to most chemicals except oxidising acids, halogens and certain ketones. LDPE is attacked by oils and greases - HDPE is far more resistant in this respect.

PE sheet can be both fabricated and thermoformed. Similar observations can be made with respect to vacuum forming of PE materials as for PP (i.e. shrinkage, narrow processing window, extended cycle times etc.) owing to their semi-crystalline nature.



Polyethylene (PE)

Identifying Polyethylene

PE materials can be identified as follows:

- Density: floats on water.
- Flame test: burns with a yellow flame, producing molten, flaming droplets (is not self-extinguishing).
Smell produced similar to that of a burning candle on extinguishing flame.
- Has 'waxy' feel.
- Insoluble in most organic solvents

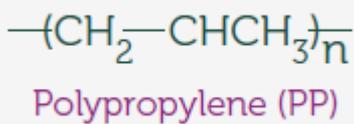
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Polypropylene (PP)

Polypropylene (PP), unlike ABS or polystyrene, is a semi-crystalline material. It also has a lower density (0.90g/cm³), higher softening point (and hence a higher service temperature) and excellent chemical resistance. Although PP exhibits good impact strength this falls off rapidly at temperatures below 5°C. Owing to its crystalline nature high shrinkage rates of between 1 to 2.5% are observed.

Although the majority of PP sheet is used for fabrication purposes some thinner gauge sheet is being thermoformed for use in such applications as thin-walled packaging.

The principle difficulty in successfully thermoforming PP is its narrow thermoforming window, i.e. its elastic range covers only a small temperature band and accurate temperature control is an essential prerequisite. Additionally webbing can be a problem owing to sheet sagging due to the poor mechanical strength of the polymer in its plastic phase.



Overall cycle times are longer with PP than compared with the amorphous polymers because of the large quantities of heat that have to be supplied and removed during the forming process.

Identifying PP

PP can be identified as follows:

- Density: floats on water.
- Flame test: burns with a yellow flame, producing molten, flaming droplets is not self-extinguishing. Smell produced similar to that of a burning candle on extinguishing flame.
- Can sometimes be flexed repeatedly without cracking along bend line.
- Has 'waxy' feel.
- Insoluble in most organic solvents