Thermoplastic composites

Definition

By definition, a thermoplastic is a material based on polymer (macromolecular compound) which can be shaped, in a liquid (viscous) state at a temperature either higher than its glass transition temperature (Tg) (amorphous thermoplastics) or higher than its melting temperature (Tm) (semi-crystalline thermoplastics). In terms of microstructure, it is composed of long, linear or branched molecules, but which are chemically separated from each other.

In contrast, a thermoset is a polymeric resin material which can, in principle, only be shaped once during its synthesis. In terms of microstructure, it comes in the form of a continuous network of atoms chemically linked to each other by strong bonds (covalent). It can be considered as being composed of a single giant macromolecule. This explains why it can only be shaped once during its synthesis. Below its Tg, it is generally hard and brittle (fragile). Above its Tg, depending on the crosslink density of the network, it is hard and tough (dense network) or very soft (loose network); in the latter case, it is referred to as elastomer or rubber (fig 1).

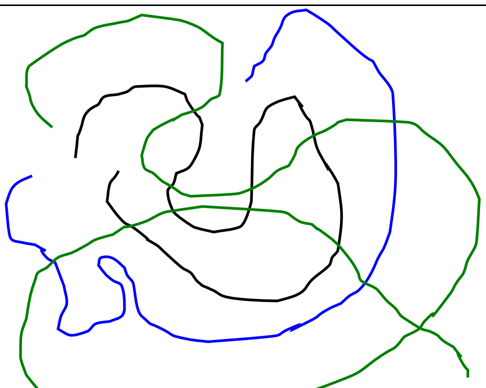
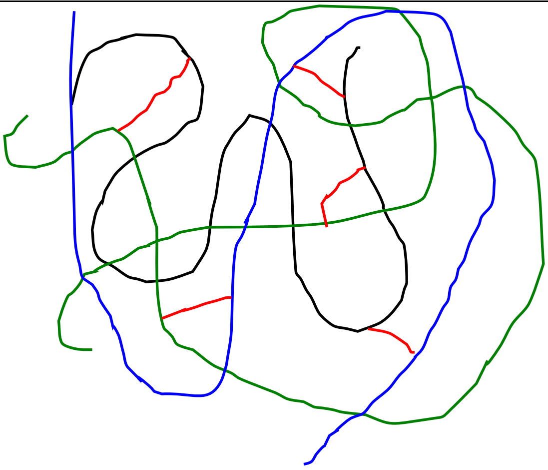
 Thermoplastic: independent chains	 Thermoset: network (in red: bridges between chains)
 Example: polyethylene bag	 Example: rubber tyre

Fig 1: thermoplastic and thermoset microstructures

Usage properties

The maximum use temperature (theoretical) of a thermoplastic is, therefore, either its Tg, if it is an amorphous thermoplastic, or its Tm in the case of a semi-crystalline thermoplastic. This is however only a theoretical limit because the elasticity modulus E (stiffness) of a semi-crystalline thermoplastic decreases significantly when its temperature exceeds Tg, i.e. much lower than Tm. Fig 2. shows the variation of the E modulus of an amorphous thermoplastic and a semi-crystalline thermoplastic with the temperature.

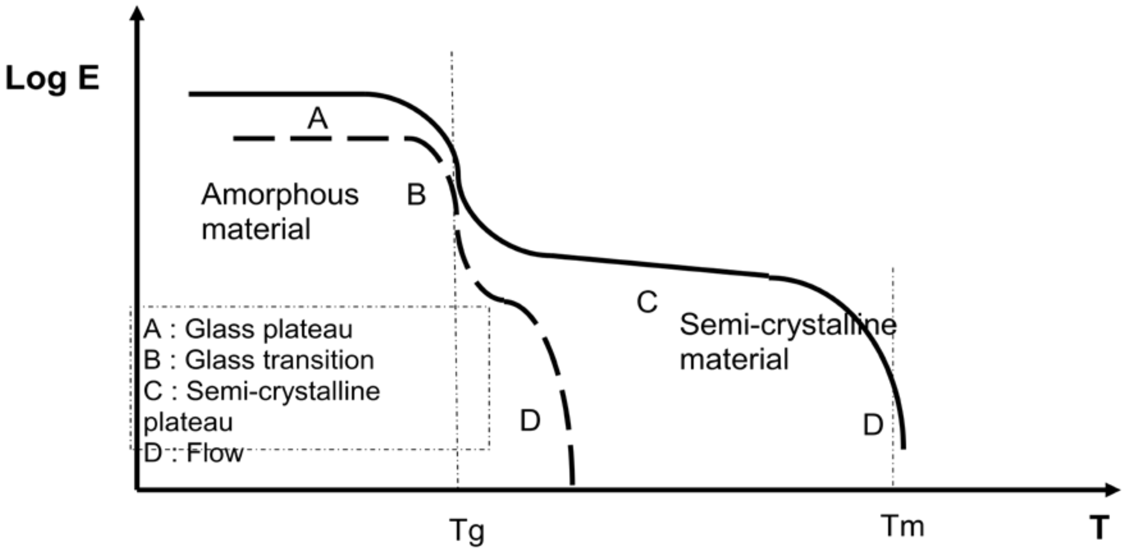


Fig 2. logE /(T°) curve for amorphous and semi-crystalline thermoplastics.

It is particularly advantageous to reinforce a semi-crystalline thermoplastic material with fibres (for example), thus to form a composite, as this allows a considerable increase of E above Tg, enabling therefore the material to be used under high stress (as a rigid material) at a higher temperature. (Fig 3)

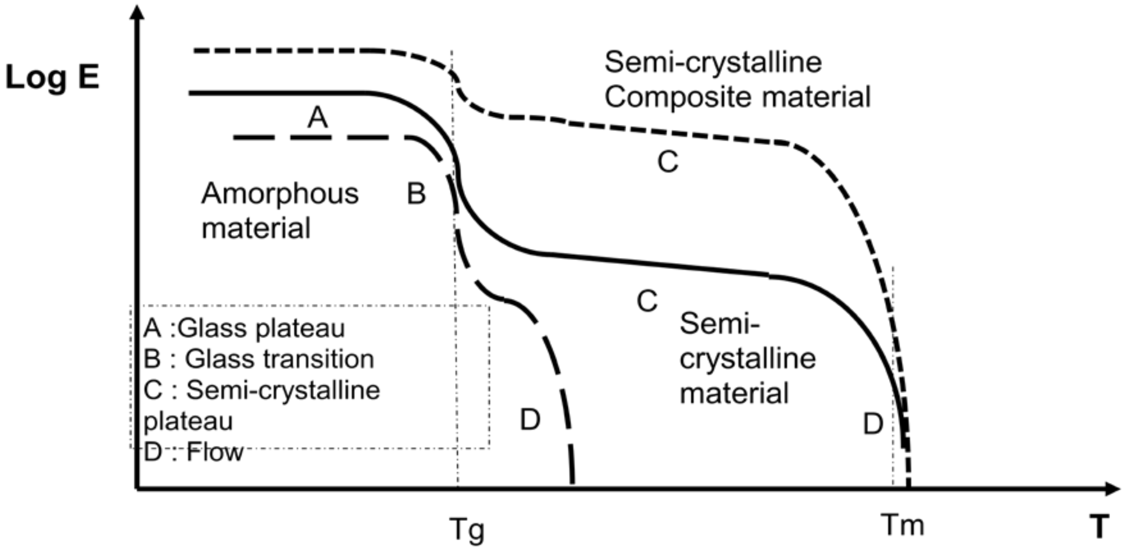


Fig 3. logE /(T°) curve for semi-crystalline thermoplastic reinforced with fibres.

Benefits

The main advantage of thermoplastic composites compared to thermosets, therefore, is that it is possible to process them (and reprocess or recycle them) in their molten state. However, in the melt, their viscosity is several orders of magnitude higher (500 to 1000 times) than the one of thermoset resins.

With few exceptions (ring-opening polymerisation or ROP as in the case of polyamide 6 RRIM[1], or c-BT, or APLC-12[2]...) polymerisation is not performed in the mould during processing, but in a preceding synthesis stage. The techniques for processing thermoplastic composites are therefore very different from the techniques applicable to thermosets.

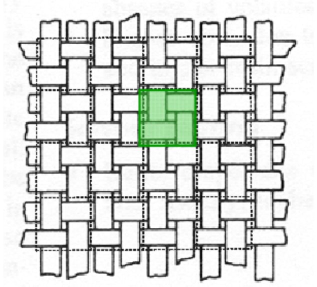
So to process thermoplastic composites, it is generally necessary, first of all, to laminate and/or melt them in a processing device such as an extruder or in an injection moulding press. Due to the high shear forces that the material is subjected to by those systems it is not possible to incorporate continuous fibres (long) into the polymer matrix by these techniques. They are instead cut into (very) short or even ground fibres.

We must therefore distinguish thermoplastic composites with long fibres, which have to be processed by special techniques, for limited production (± 1000 units/year) and short fibre thermoplastic composites, which can be processed using conventional techniques of mass production (> ± 10000 units/year) (extrusion, injection, ...) suitable for thermoplastics.

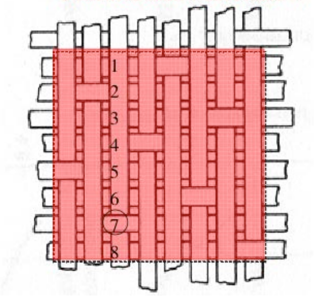
Long fibre thermoplastic composites

To process long-fibre thermoplastic composites, the most common method is to produce ribbons or laminates (or prepregs) of polymer-coated fibres. These "prepregs" are then aligned or woven by way of different geometries to make preforms (fig 2). These preforms are shaped in the press (compression) at temperatures sufficient to allow the polymer to fill all the voids. This gives either finished pieces or sheets that can still be thermoformed.

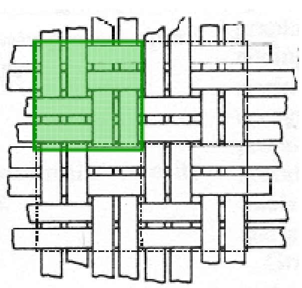
Plain weave



8-harness satin weave *base 3*



2x2 basket weave



1 Mazumdar S.: Composites Manufacturing: Materials, Product, and Process Engineering (2001), Brown M.W.R, Johnson A. F., Coates P. D. Reactive Processing of Polymers (1994)

2 www.eirecomposites.com

1/3 Twill (right handed) 3/1 Twill (left handed) 5-harness-satin base 2

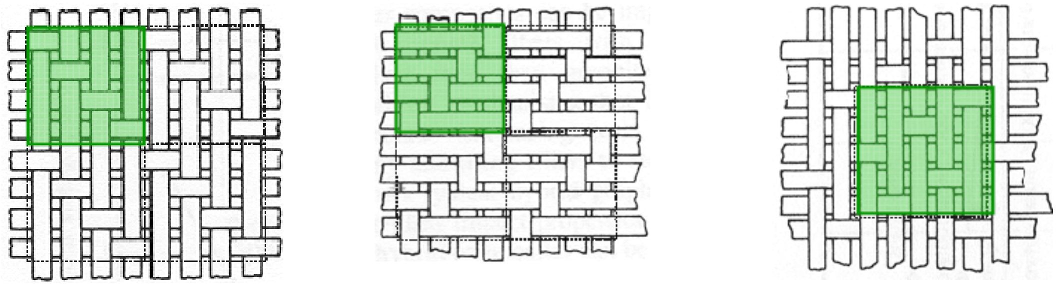


Figure 4: Examples of woven prepregs

Processing thermoplastic composites requires working at high pressure, and thus requires more robust and complex tooling than thermosets. Moreover, because the thermoplastics have to be worked at high temperatures they require more energy for their processing. In contrast, thermoplastic composites also have different maximum use temperatures which are often lower than for thermosets.
Alongside the processing of thermoplastic composites as "prepregs" the process of "comingling" should also be mentioned which consists of producing threads made up of reinforcing fibres and thermoplastic polymer fibres (Fig. 5). Preforms made using these threads can be shaped at temperatures where the molten thermoplastic is in the form of long-fibre thermoplastic composites.

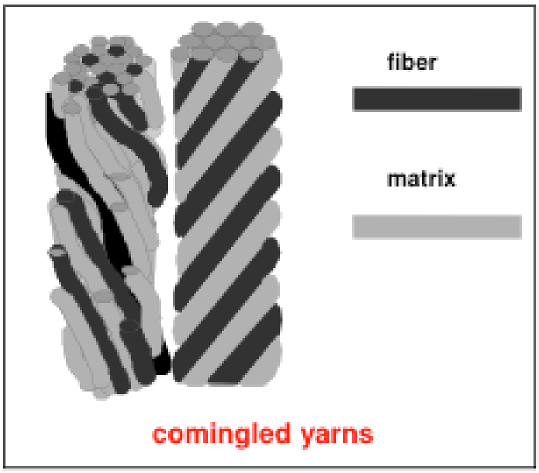


Figure 5: "Comingled fibres"

Table 1 lists some thermoplastics commonly used as matrix composites with their Tgs, Tms and processing temperatures.

Matrix	Morphology	Tg (°C)	Tm (°C)	T° process(°C)
PBT	Semi-cryst.	56	223	250
PA-6	Semi-cryst.	48	219	245
PA-12	Semi-cryst.	52	176	224
PP	Semi-cryst.	-20	176	190
PEEK	Semi-cryst.	143	343	390
PEI	amorphous	217	/	330
PPS	Semi-cryst.	89	307	327
PEKK	Semi-cryst.	156	306	340

Table 1: Thermoplastics used as matrix composites

An important advantage of thermoplastic matrices is their greater degree of flexibility than thermoset matrices. Compared with thermoset composites, this greater flexibility gives thermoplastic composites better impact resistance and better strength after impact. This is also why thermoplastics are now blended, under certain conditions, into formulations of thermoset composites[3], but the proportions remain limited, which does not therefore make them, strictly speaking, thermoplastic composites.
Thermoplastic "prepregs" can also be processed using certain techniques that are similar to "prepregs" based on thermosets, such as filament winding, calendering or pultrusion.
In addition to simple compression, preformed composite sheets can themselves be processed using techniques similar to the thermoforming of thermoplastics, such as moulding by diaphragm, hydroforming or shaping via a rubber stamp. All three can be sketched out as in Fig 5.

[3] Dumont D., Thermoplastic as nanofiller carrier into epoxy resin:: Application to delivery of carbon nanotubes or layered clay in composites processed by RTM. Thèse, Louvain)-la-Neuve, 2012

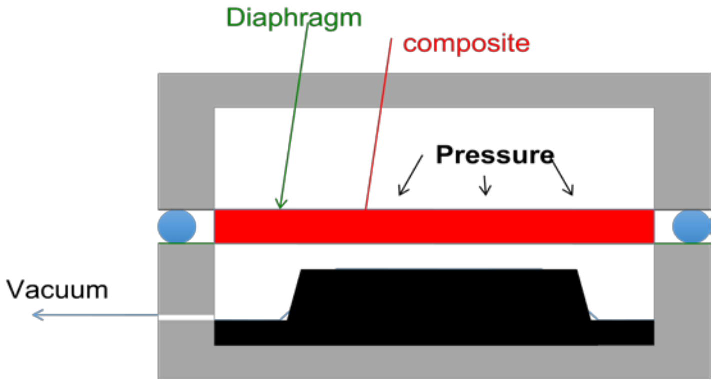
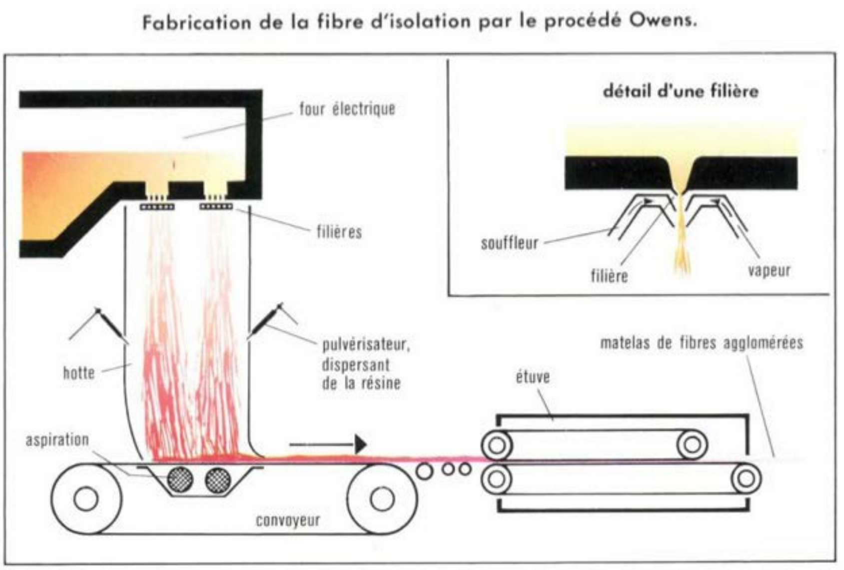


Fig 5: Shaping sheets of thermoplastic composites[4] by diaphragm. For hydroforming, pressure is provided via a hydraulic fluid, for the rubber plug method the entire upper area is replaced by a rubber plug.

As for all composite materials containing thermoset or thermoplastic matrices, it is only possible to benefit from the mechanical properties of the reinforcement (fibre) if there is an efficient force (stress) transfer between the matrix (here, the polymer material) and the reinforcement. For this, a good adhesion between the matrix (polymer) and the reinforcement (fibre) is essential. This adhesion may be of physico-chemical origin (adsorption of the polymer molecules (or parts of molecules) on the fibre by electrostatic attraction between dipoles, ...) or, more often, of chemical origin (chemical bonds). For this purpose, the fibres (or other reinforcement) are often treated with various additives to cause a chemical reaction between the polymer matrix and the solid surface of the reinforcement. These reactive additives are included within the treatment of fibres the so-called "sizing" (fig 4).

[4] Kausch H.H.Advanced Thermoplastic Composites, Hanser, 1992



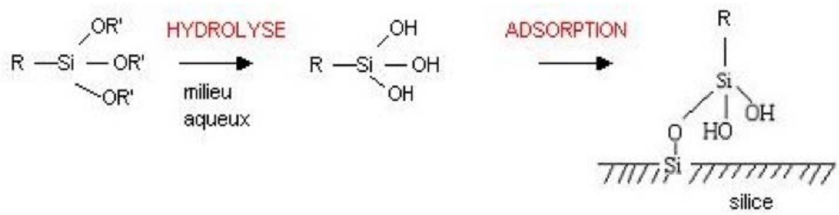


Figure 4: Scheme of the production of glass fibre sized by resin and the chemical coupling owing to the sizing.

Short-fibre thermoplastic composites

Short-fibre composite materials have the advantage that they can be processed using techniques adapted to thermoplastics such as extrusion, injection, etc.
Nevertheless, because of the passage of the material through these machines, most of the time, the fibres are reduced to small dimensions, in which case the materials are more frequently referred to as reinforced polymers rather than composite materials. However they are actually composites. To obtain an effective reinforcement in the direction of fibre axis it is nevertheless essential that the fibre retains a minimum length below which it no longer provides efficient strengthening. A "critical length" is determined for this, which is the minimum length required to transfer the load experienced by the composite in the direction of the axis of the fibre to the latter. Fibres which are longer than the critical length make an effective contribution to the resistance of the composite. as the critical length can be defined by the formula:

$$l_c = \sigma_f d / 2\tau$$

Where l_c is the critical length, d is the diameter of the fibre, σ_f is the tensile strength of the fibre and τ resistance to the shear matrix. Generally, critical lengths of approximately one mm or less are obtained. It is therefore extremely advantageous to reinforce thermoplastic matrices with “chopped” (cut) fibres, providing their processing does not reduce their lengths to values that are too low, around the critical length. But this critical length is directly proportional to the diameter of the fibre and so it makes more sense to refer to a critical aspect ratio (l_c/d). The aspect ratio l/d below which the reinforcement loses a significant part of its efficiency is generally in the region of 10 to 100.

Life cycle of thermoplastic composites

One of the great advantages of thermoplastic composites which is becoming nowadays increasingly important is their recyclability. Short-fibre thermoplastic composites can, for example, undergo several cycles of processing before the critical fibre length is reduced too much. Thus, these composites behave more like "ordinary" thermoplastic materials rather than composites. Even long-fibre thermoplastic composites can be reprocessed after grinding like the materials that have been reinforced by short fibres.
This recyclability is particularly important when, as in the automotive field, stringent standards are imposed on the recyclable nature of the materials used.

This article forms part of a series of technical articles aimed at industrial manufacturers wishing to increase their knowledge of the field of composite materials. It was produced within the Composites project (www.pluscomposites.eu).