Plastics Topics – Fillers for enhanced performance

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1. Introduction

Fillers and reinforcements have a long history in plastics processing and thermosetting polymers such as Bakelite (one of the first commercial plastics) would be not have been commercially viable without the use of reinforcing fillers. Equally rubber, without the addition of carbon black (a reinforcing filler), would be a sticky material of great interest but of absolutely no use in the manufacture of car tires. Despite this, ‘filler’ is an emotive word and most people immediately think of fillers in the negative sense, i.e., as a component added to reduce cost, whereas fillers can do much more than simply reduce cost. The term ‘reinforcement’ has a much more positive ring to it but the reality is that most reinforcements are also fillers in some manner.

Fillers are added for a variety of reasons but the primary reasons are:

- To modify and enhance the properties of the base polymer.
- To reduce the cost of the final plastic material.
- To improve the processing of the base polymer.

One way of dividing up the many types of fillers used in shown in Figure 1. This clearly differentiates between fillers, functional fillers and reinforcements.

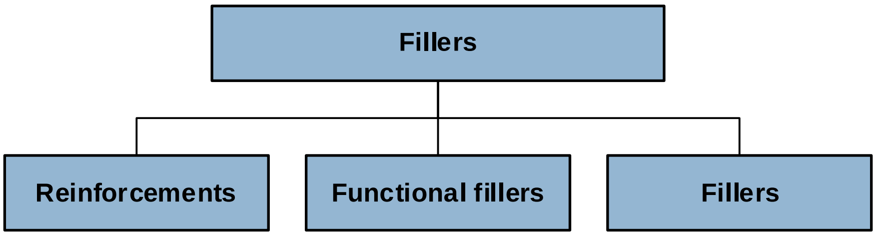

Figure 1: The types of fillers

A more accurate division of the types of fillers is shown in Figure 2, which shows that fillers cannot be easily divided into discrete groups. The family of fillers is much more of a continuum than a set of discrete groups and, even then, the position on the continuum depends on the particular polymer and filler combination. As in gardening, a weed is simply a plant growing in the wrong place (or a plant whose virtues have not yet been appreciated!).

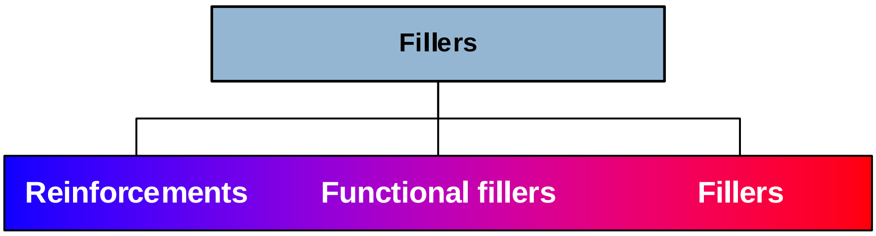

Figure 2: The types of fillers – a more accurate description

As a simple example, straw was traditionally added to mud bricks as both a filler (it is easy to obtain and is cheap) and as a reinforcement (it added strength to the bricks). In terms of Figure 2 it is neither a pure filler nor a pure reinforcement – it is a functional filler that both fills and reinforces the basic mud brick. This Plastics Topic concentrates on the functional aspects of fillers – those fillers in the middle of the continuum that cannot be classed as reinforcements but which enhance the performance of the base polymer rather than simply add bulk and reduce cost. This is not a restriction because most fillers can be considered to be functional if used with the correct base polymer.

2. Filler types

Reinforcements

One definition of a reinforcement is that it is stronger than the base polymer materials and has an aspect ratio of length to thickness that is greater than 1 and is typically greater than 200. When reinforcements are used the resulting combination of polymer + reinforcement is sometimes termed a 'composite' material.

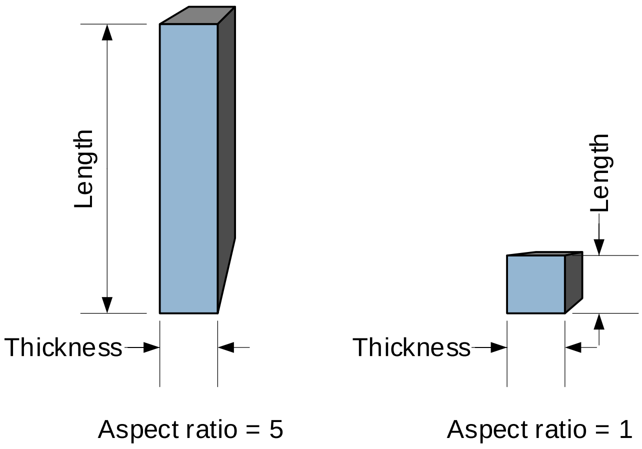

Figure 3: The aspect ratio for two fillers, if the aspect ratio is greater than 200 the filler is more properly classed as a reinforcement.

It is typically thought that adding reinforcements will improve the mechanical properties. This is true for some mechanical properties such as tensile strength and flexural modulus, but it is also true that adding reinforcements will decrease other mechanical properties. Adding 10% glass-fibre to Nylon 6 will increase the tensile strength by around 50% but will also decrease the Izod impact strength by around 25%. This is because natural nylons show a tough fracture (large amounts of deformation at the fracture surface) whereas glass-fibre filled nylons show brittle fracture. If the specific requires high impact strength, then adding glass-fibre reinforcement may not be the way to go.

Reinforcements work by bonding tightly to the polymer and then distributing applied loads over many polymer chains along the length of the reinforcement. Specific surface treatments are often required to achieve a good bond between the reinforcement and the polymer matrix.

Most reinforcements become oriented during processing and make the mechanical properties of the part anisotropic (they vary with direction) and typically mechanical properties of fibre reinforced parts are much greater in the direction of the fibre orientation than in directions normal to the fibre orientation.

Extending fillers

Fillers can also function as simple extenders that can significantly reduce the cost of the product with little or no effect on the mechanical properties at reasonable addition rates. The volume addition rate for simple extenders is often limited because, whilst low addition rates may marginally improve properties, the use of high addition rates (>40%) can start to significantly reduce the mechanical properties. Often the first property to suffer in this case is the impact strength where the addition of high volumes of extending fillers can lead to significant reductions in impact resistance.

Functional fillers

Functional fillers are those that significantly improve a specific material property (as opposed to simple extension of the material). Most fillers can be considered to be functional fillers when used with an appropriate polymer matrix.

3. Filler types

Fillers can be subdivided on the basis of several criteria and these divisions provide an insight into both the mechanism of property enhancement by fillers and broad guidance on the selection of the most appropriate filler.

Chemistry

Subdividing fillers according to their basic chemistry and structure shows the wide range of materials that are used as fillers and reinforcements – this type of classification is shown in Figure 4:

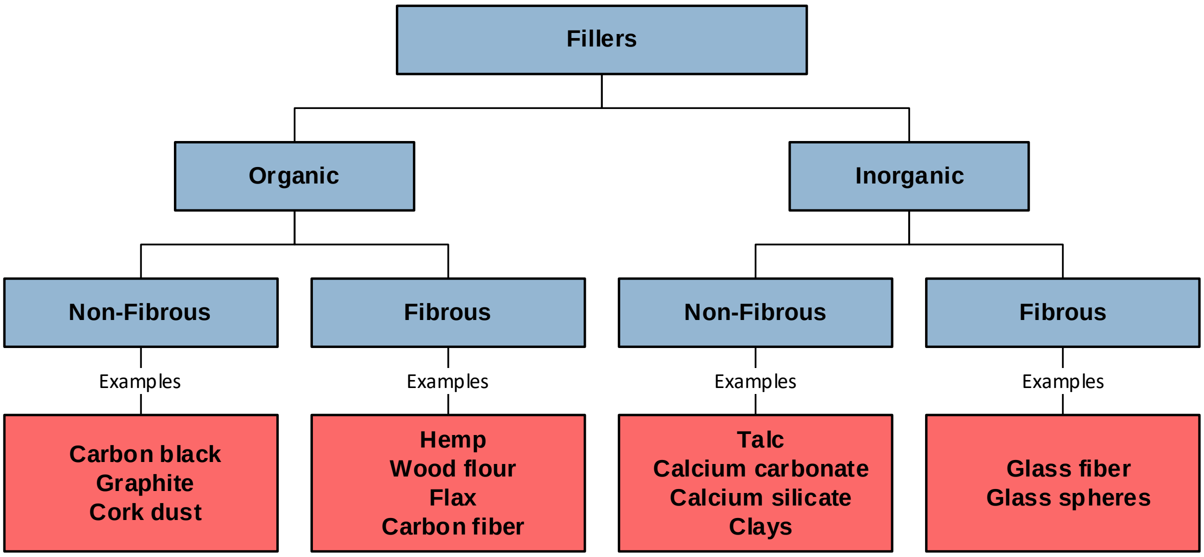

Figure 4: Fillers divided by chemistry

This shows that fillers are not restricted to a single chemical structure. The range of fillers is both broad and deep.

Size/Aspect ratio

Subdividing fillers according to their aspect ratio shows that fillers are not one simple structure but can vary widely in shape and form – this type of classification is shown in Figure 5:

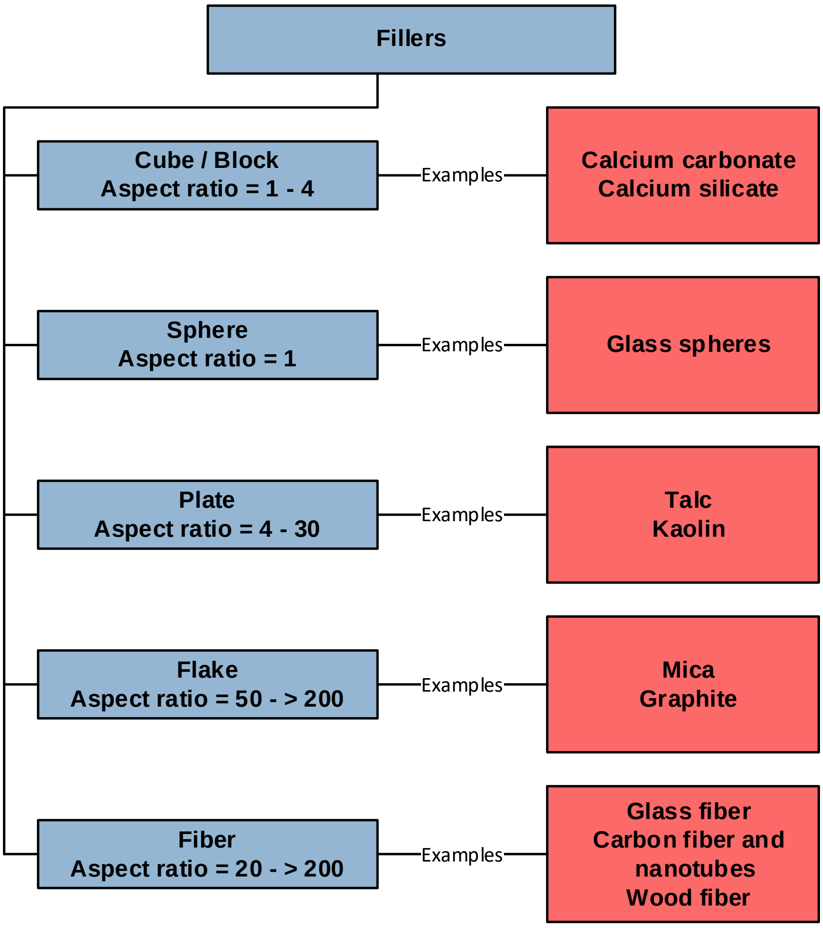

Figure 5: Fillers divided by aspect ratio

It is important to realize that no single aspect ratio (shape or form) is best – the filler must always be chosen for the application.

Functionality

Subdividing fillers according to their main functional effect on the base polymer is also possible and reveals a range of properties that can be enhanced by fillers – this type of classification is shown in Figure 6.

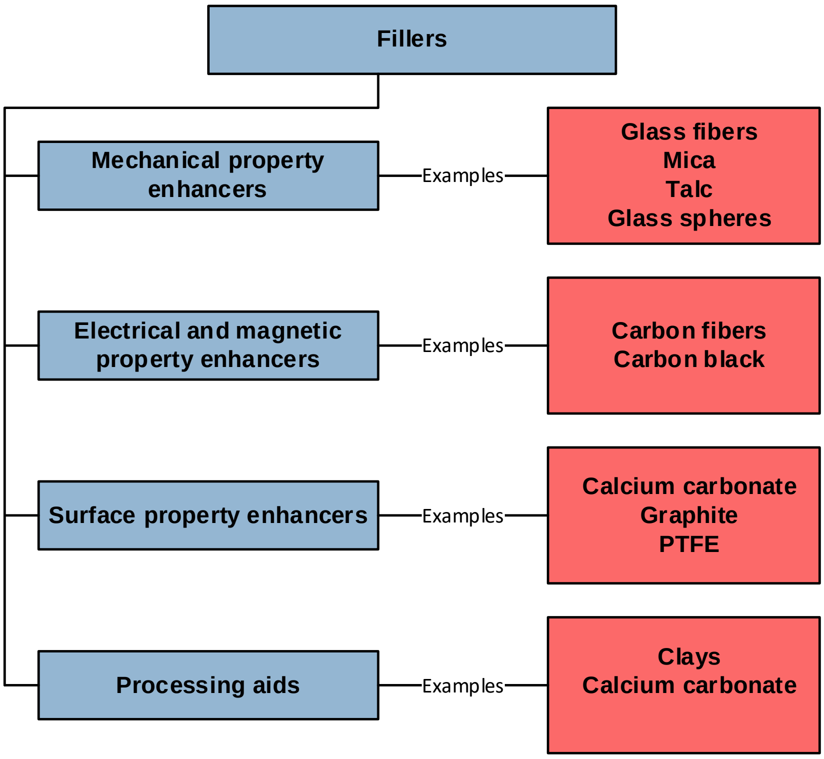

Figure 6: Fillers divided by main function

When fillers are considered in this manner it is important to realize that fillers do not act in isolation:

- The property enhanced by the filler and the degree of enhancement (or not) is also highly dependent on the polymer matrix that is being used.
- Fillers never act on a single property to the exclusion of the other properties – a filler used to enhance one mechanical property could also have a detrimental effect on other mechanical or materials properties.

4. Desirable characteristics

The desirable characteristics of a filler are relatively easy to describe but are more difficult to obtain in practice from the range of available fillers. Inevitably, in real life, choosing a filler will require trade-offs, despite this, the ideal characteristics are:

1	Maximizes the desired physical property: This will depend strongly on the application requirements and the specific physical property that is desired.
2	Low cost and freely available: Fillers should not generally be more expensive than the polymer matrix although in the case of some nano-fillers this is not the case.
3	Good wetting properties relative to the base polymer: The filler needs to be wettable by the polymer matrix to enable load transfer to the filler and good mixing. In some cases, relatively poor fillers can be significantly improved by surface treatment.

4	Good distribution of particle size and shape: Fillers that have a wide distribution of particle sizes and shapes will not provide consistent property enhancement as the enhancement will vary throughout the bulk plastic.
5	Good surface area to volume ratio: Fillers will become more effective in property enhancement if the surface area (and hence the contact with the polymer matrix) is maximized with regard to the volume of the filler. As a general rule the smaller the filler particles then the larger the enhancement of properties possible.
6	Low agglomeration tendency and good dispersion properties: The filler needs to be evenly dispersed in the polymer matrix even at low addition volumes. Fillers that agglomerate give poor property enhancement.
7	Good heat resistance at polymer processing temperatures and non-flammable: This is particularly important for organic fillers that can degrade at high processing temperatures such as those required for processing fluorocarbons.
8	Low moisture absorption and low solubility in water and common solvents: Fillers should not absorb moisture from the environment otherwise the compound may need additional drying before use, e.g., talc-filled PP can need drying and this increases costs. A low solubility is also necessary to prevent fillers from being leached out of the polymer matrix.
9	Lack of impurities: Some mineral fillers need careful pre-treatment to remove impurities that could reduce the property enhancement or damage processing equipment
10	Low or no odour: Fillers should not add odour to the compounded plastic.
11	Good colour properties and retention: Fillers should enable the use of colorants and retain colours when exposed to the environment. This requires some matching of the refractive index and good opacity if a dense colour is required.
12	Good heat and chemical resistance: Fillers should not chemically or thermally degrade during either processing or normal application temperatures.

Table 1: The ideal characteristics of a filler.

5. Common fillers

There is a wide range of fillers available and their interactions with the equally wide range of base polymers make the choice of a specific combination heavily reliant on the experience of the supplier. Some of the most common fillers are:

Talc

Talc is a common filler used with many polymers such as PP to both extend the base polymer and to reduce the product weight. One of the major disadvantages of talc is that water absorption at room temperature can make additional drying necessary for some normally non-hygroscopic materials.

Clay

Clay is really a generic name for a variety of crystalline and non-crystalline materials such as kaolinite, montmorillonite, and illlite that are purified and filtered to obtain a uniform particle size. Clays have traditionally been regarded as cheap extender type fillers but interest in clays for property enhancement has been renewed by the development of 'nanoclays' – where ultra-pure and very small particle size clays have been found to have greatly improved properties compared to the traditional clay fillers.

Calcium carbonate ($CaCO_3$)

Calcium carbonate is the classic 'chalk' filler and is obtained from either mining of chalk and limestone or produced chemically (precipitated calcium carbonate). It is common for calcium carbonate to be treated with stearic acid or stearate salts, e.g., calcium stearate, to improve the properties of the filler.

Glass fibres and spheres

Glass is an excellent filler and meets many of the ideal characteristics of a filler. The use of glass as both a reinforcement (in the fibre form as either short or long glass fibres) or a filler (in the form of small glass spheres) is growing rapidly as new production techniques are developed to both produce the various glass formats and also to coat or treat the glass to improve the adhesion between the glass and the polymer matrix.

Wood flour

The use of wood flour and wood fibres as fillers has expanded rapidly in the past decade with the introduction of the new wood plastic composites. These materials can be regarded as heavily filled (up to 70% wood) plastics or as a new generation of improved wood products or even as a new industry in the materials world. The major technical achievement in the development of these materials was the production of coupling agents that allow a hydrophilic material (wood) to be intimately mixed with, and bonded to, a hydrophobic material (the base polymer – typically PVC, PP or PE). This new industry is bridging the gap between the plastic and wood product and is destined to be one of the most interesting developments in the materials world in the past 50 years.

Nano-fillers

The current worldwide interest in nano-technology has not been neglected in the world of fillers and the development of nano-fillers is an area of intense research in polymer technology. Nano-fillers are microscopic fillers that have a very high surface to volume ratio and also a high aspect ratio to provide a far greater surface interaction between the filler and the polymer. The much greater surface area of the filler increases the potential for property enhancement and provides a much more uniform dispersion of the filler in the matrix.

Nano-fillers include nanoclays, nano-silicates, carbon nano-tubes and ultra-fine TiO2. The applications for these recent developments are still being explored but range from structural materials (where the nano-fillers increase stiffness and strength) to barrier packaging (where the nano-fillers improve strength, resistance to grease and oils and reduce oxidation).

6. Special fillers

Functional fillers may be considered to be a special case of general additives for property enhancement and in many cases special fillers can be used to modify not only the mechanical properties but also to enhance other properties. Fillers can be used to enhance the properties of plastics in fire, act as surface property modifiers, act as processing aids and to act as bioactive agents in the polymer matrix. The most important special fillers are used to improve radio-opaqueness and to improve electrical conductivity:

Radio-opaque fillers

Fillers can be used to make medical products radio-opaque for easy detection under radiation. The most common fillers used (in approximate order of usage) are barium sulphate, bismuth subcarbonate, bismuth trioxide, bismuth oxychloride and finely ground tungsten. As with any filler, the compatibility of these products with a selected polymer matrix and polymer processing conditions must be checked to ensure that the correct filler is used.

Conductive and magnetic fillers

Conductive fillers such as metal or other conductive fibres can be used to improve the electrical conductivity of plastics and this type of filler is typically used for applications where EMI shielding. Typically, carbon black, carbon fibres and metal fibres are used to improve EMI shielding or to dissipate static electricity.

7. Summary

Fillers might initially appear to be the least interesting component of plastics but the reality is that fillers deliver enormous potential benefits by modifying and enhancing the properties of the base polymer.

Two of the most exciting developments in polymer processing are firmly based on the development and commercial exploitation of new fillers. These developments have the capacity to radically change the world of plastics processing – not many other components of plastics have that much potential. The development of fillers is anything but boring.