

3. POLYMERIC COMPOSITES

Fillers are used as volume extenders or to improve physical and mechanical properties of polymers. Fillers used to increase the bulk volume of a polymer are known as extenders. Functional fillers, on the other hand, improve mechanical or physical properties. They can be subdivided into functional additives and reinforcements. [7] The former improve physical properties such as thermal or electrical conductivity. Reinforcements improve mechanical properties such as heat deflection temperature, stiffness, impact strength and breaking strength. [7,8]

Mica can act as either a functional filler or as reinforcement. Mica is chemically inert, except to concentrated sulphuric acid and hydrofluoric acid. Muscovite is transparent to UV radiation while phlogopite is opaque.[5] Therefore, phlogopite can contribute to the UV stabilization of the polymer to which it is added. Mica can withstand high temperatures and will not support combustion. [5] The addition of mica can also improve the fire resistance of polymer products such as wall boards, that shield the flammable material from the flame. [10] Mica can also delay, to some extent, the onset of thermal degradation of thermoplastics to which it is added.[9] The thermal resistance of a filler-polymer composite is due to a combination of good structural integrity, low thermal conductivity of the filler and endothermic decomposition pathways. These effects slow down heat transmission through the composite. [11]

Usually it is not possible to optimise the reinforcement properties, e.g. impact strength and stiffness independently. These properties are not affected in the same manner; some may improve while others actually decrease [8], but this depends on the type of filler and polymer used. Therefore it is important to clearly define what is meant by reinforcement.

3.1 Reinforced polymers

3.1.1 Mechanism of reinforcement

They are grouped into one-dimensional (e.g. fibres), two-dimensional (e.g. plates) and three-dimensional (e.g. spheres). [15]

The reinforcing action of functional fillers can be attributed to several factors: [7]

- the large difference in stiffness and strength between filler and matrix
- the volume that the filler particles take up
- the formation of chemical bonds between filler and matrix
- slipping that may occur at the filler matrix interface.

Fillers, unlike typical polymers, are characterized by a very high degree of dimensional stability. This implies that the volume that the filler particles occupy is not accessible to the polymer chains. Furthermore, the polymer chains tend to adsorb on the filler surfaces. The segments may attach to the surface through primary and secondary valence bonds. This restricts the motion of the polymer chain molecules as the number of available chain conformations is reduced. Thus polymer segments adjacent to the surface of the filler particles are immobilized. This also leads to the formation of a zone directly at the filler surface that is more ordered than the rest of the polymer matrix. Therefore the filler particles act as physical cross-links preventing chain slippage thus stiffening the material as a whole. [7]

Important parameters that influence the mechanical behaviour of reinforced polymers are:

- the shape and orientation of the reinforcing agent [12]
- particle size [13] and its distribution [14]
- the filler concentration [13]
- the level of interfacial adhesion [13]

Shape of the reinforcing agent

The five common filler shapes are summarized in Table 2. [8] They are grouped into three categories according to their dimensionality, i.e. one dimensional (e.g. fibres), two dimensional (e.g. flakes) and three dimensional (e.g. spheres). [15]

When optimum reinforcement with respect to moduli is desired, the chain confinement effect of fillers implies that the area-to-volume ratio (A/V) should be maximized. For fixed particle volume, the A/V ratio for a sphere is fixed. However, for fibres and flakes it can still be changed by manipulating the aspect ratio.[8] The implication is that both the size and shape determine the surface area of the filler particles. [8,15]

Table 2: Summary of five common filler shapes. [8]

	Group				
	3-D			2-D	1-D
Particle class	Sphere	Cube	Block	Flake	Fiber
Description	Spheroidal	Cubic Prismatic	Tabular Prismatic	Platy Flaky	Fiber
Examples	Glass- spheres Micro- spheres	Calcite Feldspar	Calcite Silica Barite Nephelite	Kaolin Mica Talk Graphite	Wollastonite Tremolite Wood flour
Typical A/V^*	High	High	High	Low	Medium

* Area to volume ratio

Mechanical properties, including shrinkage, in materials reinforced with spherical particles are almost isotropic. Reinforcement with spheres may lead to increased compressive strength, as well as improved flexural modulus, but it tends to decrease impact strength.

[7]

In fiber reinforced polymers the fibre orientation is very important as it allows anisotropic reinforcement of the polymer. However, random fibre orientation leads to near isotropic mechanical properties. Fibre reinforcement leads to an increase in tensile and flexural strength in the orientation direction. Plane isotropy is also possible but it is more common to use fibres for unidirectional reinforcement. The fibre aspect ratio (length-to-diameter ratio) also affects the reinforcement action. With increasing fibre length more surface area is available for interaction between the polymer chains and the reinforcement. Long fibres allow better stress transfer between matrix and reinforcement.

Particle size and distribution

Unfortunately, anisotropic fibre orientation also leads to anisotropic shrinkage of parts during moulding. The differentials in shrinkage may lead to warping of moulded parts. [7]

Effect of plate-like fillers on shrinkage effect on mechanical properties

The effect of plate-like reinforcements is intermediate between that of spheres and fibres. The flaky shape of the fillers leads to modification of the polymer properties in two directions. Once again the aspect ratio of the flake particles plays a significant role; higher aspect ratios leads to better reinforcement owing to the higher surface area generated. The increased surface area leads to stronger interaction between the polymer chains and the surface of individual filler particles. Reinforcement with flakes leads to an increase in tensile and flexural strength [7], but compared to fibres the reinforcement effect is less. However, overall shrinkage is reduced and part warping is less likely. Furthermore, the presence of resin-rich regions, voids or flake imperfections, as well as poor adhesion and inhomogeneous sites, will lower the strength of a composite. [16]

Effect of two dimensional orientation on barrier properties

Two dimensional orientation with platelet fillers leads to a lamellar micro structure. Owing to the increased tortuosity of the diffusion path, such materials exhibit reduced gas and vapour permeability. Important factors that control barrier properties are platelet size, aspect ratio, concentration, size distribution, orientation and interfacial adhesion. [12] Lamellar morphologies may be induced through flow orientation, in processes such as drawing or calendering. [12] Apart from flow induced orientation, self orientation comes into play at high filler volume fractions.

Commercially available mica flakes tend to be highly irregular with respect to their diameter and thickness. When mica is used at low dosage levels, the alignment is random if not specifically orientated by external means.

Järvelä and Järvelä [8] found that combinations of various different filler shapes can provide improved reinforcement. For example, the combination of fibres and platelets showed strong synergy with respect to the flexural strength in polypropylene. [8]

Particle size and distribution

In general particles that are too large may act as points of discontinuity in the composite and may therefore have an adverse effect on mechanical properties. The ideal filler thus has a high aspect ratio and a size distribution with a particle size cut-off at the higher end.

Busigin et al. [17] found that the modulus of mica-filled polypropylene composites is dependent on the flake aspect ratio, whereas the strength is influenced more by the size, i.e. the flake diameter. This implies that in order to maximise both modulus and strength, smaller particles with a large aspect ratio are to be preferred. [17]

Filler concentration

At low filler contents (<10% by mass) reinforcements have little effect on material properties. [8] Mechanical property enhancement is most dramatic at the higher levels of filler content. [18] In general, adding fillers reduces impact strength, but improves rigidity and breaking strength. Thermoplastic polymers are rarely filled beyond 30% by volume. Higher loadings are difficult to process and lead to a loss of mechanical properties. Ultimate properties, such as tensile strength, are very sensitive to complete filler wet-out by the polymer. This necessitates the use of coupling agents at high filler loadings.

Adhesion

It is generally acknowledged that different mechanisms of adhesion work, alone or sometimes together in a particular system. Presently four mechanisms are generally recognized: mechanical interlocking, interdiffusion, electrostatic attraction and chemical interactions. These forces work at different scales of distance between the materials: from the atomic scale for chemical bonds to an undetermined scale in the case of mechanical interlocking. [41]

Situations where mechanical interlocking may be relevant are those when the solid material are very porous and when the adhesive solidifies it forms a sort of anchoring. A similar case is that of the presence of protrusions, around which the adhesive can solidify. The question, however, remains whether mechanical interlocking is a mechanism on its own, or if it simply increases the efficiency of other mechanisms due to the increased surface area.

Interdiffusion only has relevance between two compatible polymers where chains of the one moiety diffuse, at least partially, into the other. With regards to electrostatic attraction its contribution is usually very small and only occurs when both surfaces has a nett charge. [41]

Chemical interactions between two bodies embrace a variety of forces, such as non-polar dispersion forces, dipole-dipole interactions, dipole-induced dipole interactions and the formation of true chemical bonds.

The examination of the various theories made on the basis of adhesion, and specifically referred to polymers, has shown that only those based on chemical interactions have a general character and a wide application. Since various types of interactions and bonds can be established, the occurrence of them strictly depends on the chemical nature of the materials under consideration. [41]

The performance of composites is strongly influenced by the nature of the interface between the polymer and the filler. Consequently surface modification plays a major role in the manufacturing of composites. [8,19,20,21,22] The effectiveness of the reinforcing agent depends on the aspect ratio as well as the effectiveness of the adhesion between the polymer and the filler. [20,23] If there is no adhesion, the filler particles simply represent flaws that may actually decrease the load bearing ability of the polymer. Adequate adhesion is a prerequisite for stress transfer between reinforcing filler particles and the matrix. [24]

The filler particle surface is inert and therefore chemical bonding between the polymer chains and filler particles surface usually does not occur. Several strategies are available for improving the interaction between filler and polymer. These include the use of coupling agents, surface active agents, organic surface coatings on the filler and modifying the polarity of the polymer.

Coupling agents may provide suitable bonding between the filler and polymer. They attach to the filler particle surfaces either chemically or through physical bonds such as van der Waals forces. The opposite end of the coupling agent molecule is able to chemically bond to the polymer chains. Thus coupling agents chemically bind the polymer chains to the filler particles. Good coupling agents will improve the following properties of the composite: [19]

- the wettability of the filler surface by the polymer.
- the shock absorbing and stress releasing properties of the interface
- the mechanical strength of interfacial layer.

Many different coupling agents are available. The final physical properties of the composite depend on the type and concentration of the coupling agent as well as the method and conditions used to incorporate it. [18] In addition to improving adhesion between the filler and the matrix, coupling agents also modify the rheological properties. A reduction in melt viscosity aids filler de-agglomeration and can also improve flake alignment. [18]

Conventional coupling agents include silanes, zirconates and titanates. [19] Silanes have been used as surface modifiers for mica. [8,17] Their use improves the wettability and dispersion of the filler in the matrix and eliminates voids due to uneven packing. [22]

Newman and Meyer [18] state that a ductile matrix with adequate interaction between phases is required for proper stress transmission between polymer and filler and to minimize the effect of defects in morphology. [18] In polymer composites failure may initiate in the bulk polymer, at the polymer/filler interface or within filler particle agglomerates. [16] Depending on the strength of the interfacial bonding two failure modes are possible for mica filled composites: flake fracture and flake pull-out. Flake pull-out and separation prevent full utilization of the filler's strength. [18]

Surface active agents can also be used to improve interfacial adhesion as well as the dispersion of fillers in a matrix. For example, stearic acid is used with basic fillers such as calcium carbonate. [16]

Surface coating techniques can also be used to advantage. Inubushi et al. [40] reported improved adhesion in mica filled ABS when treated with an aminimide cured epoxy resin, where it improved the flexural strength of the composite.

Finally, the affinity of non-polar polymers for the ionic fillers can be improved by incorporating polar groups on the chain. Grafting a polar monomer onto a non-polar polymer improves its adhesion to fillers. For example LLDPE can be modified by graft copolymerisation with polar monomers, e.g. acrylic acid or maleic anhydride. Typically the grafting reaction is peroxide initiated. At low dosages of monomer and initiator the tendency for cross linking is reduced, but homopolymerisation may still occur as a side reaction. [16] In the absence of adhesion only mechanical interlocking exists between the filler and the polymer. [21]

An alternative to grafting is to modify the polymer by irradiation with an electron beam or with gamma rays. This process introduces polar groups onto the polymer chains due to controlled oxidation thereby increasing adhesion ability. [25]

SEM analysis of a fractured surfaces is a powerful tool to qualitatively assess the interfacial bonding in a composite. [39] SEM photos of an epoxy / mica composite revealed smooth filler surfaces when interfacial adhesion was poor (adhesive failure). In contrast, for strong adhesion, threadlike features were visible due to cohesive failure of the polymer. [24]

3.2 Particulate composites with a polymer as binder

Reinforced polymer systems generally contain less than 50% (by mass) filler. Particulate composite systems represent the other side of the spectrum comprising much higher contents of granular fillers. [14] Here the polymer simply acts as a binder for the fillers.

3.2.1 General concepts

There are two theories that are used to describe particulate composites: the filler theory and the mastic theory. [14] The filler theory states that the composite achieves optimal properties when the particle size distribution allows maximal packing efficiency. According to the mastic theory the polymer produces a coating on each filler particle with optimal thickness. This film provides the bonding contact between the particles that leads to a stable and strong composite structure. [14]

3.2.2 Factors influencing composite properties

As in reinforced polymers the mechanical properties of particulate composites are determined by the filler to binder ratio, filler size and distribution and the degree of wetting and adhesion that is achieved between the filler and the polymer. [14]

However, processing factors also influence the properties of a composite. In thermoplastic compression moulding, these include tool design, tool temperature, preheat temperature, moulding pressure and time at pressure. Preheat temperature was found to contribute most to the final properties of a commingled glass and polypropylene composite. High preheat temperatures result in reduced polymer viscosities. This aids the impregnation of the polymer into the glass fibre bundles and allows for compaction to occur. [26] While high pressures are needed to reduce void content, pressure was a less important parameter than the preheat temperature. [26]

Sidess et al. [14] have shown that more polymer is needed to wet smaller particles than larger particles. Thus the smaller particles play an important role in determining the optimal matrix content for enhanced mechanical properties. To obtain a stiffer material dense packing is required while for compressive strength the matrix should have a measure of ductility. The results of Sidess et al. [14] showed that all the mechanical properties attain maximum values at the same particle size distribution. However, for other formulation variables this is not the case, e.g. filler to binder ratio.

4.1 The Young's modulus for lamellar composites

The available models for predicting the Young's modulus vary from empirical to highly theoretical. One of the simplest models describe the composite as alternating layers of high modulus reinforcement and a more compliant matrix. The elastic properties of these laminated composites depend on their orientation relative to the applied stress as shown in figure 1. The assumption is made that the layers are strongly bonded and this implies that the volume fraction, rather than the thickness of the individual layers determines the mechanical properties. The effective moduli when the layers are in parallel or in series