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MINERALS IN PLASTICS

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1. Industrial minerals

Industrials minerals – aka non-metallic minerals – represent a very broad range of natural or synthetic minerals, which find numerous industrial applications – applications not including the production of metal or energy. They basically include all those materials that man takes out of the earth's crust except for fossil fuel, metallic ores, water and gemstone.

In many cases, these minerals are crushed, finely ground, classified and possibly purified by various techniques (flotation, magnetic or gravimetric separation, ...), but are not subject to dissolution, chemical reduction or other chemical treatments, which are common for the minerals used in metal production. While in some applications such as glass the minerals are subsequently melted in a furnace, in other applications such as plastics, the mineral remain as such, intact with its original mineralogical characteristics throughout its "service life".

Main industrial mineral commodities and producing countries

Mineral	Global Annual Production in Tonnes (2001)	Main producing countries
Baryte	6.600.000	China, India
Bentonite	9.900.000	USA, Greece
Borates	4.600.000	USA, Turkey, Russia
Feldspar	9.280.000	Italy, Turkey, USA
Gypsum	110.000.000	USA, Iran, Canada
Kaolin	41.200.000	USA, Uzbekistan, Brazil
Phosphate	128.000.000	USA, Morocco, China
Potash (KCl)	27.400.000	Canada, Russia, Belarus, Germany
Rutile-Ilmenite	4.600.000	Australia, South Africa
Salt	214.000.000	USA, China, Canada
Silica sand	97.000.000	USA, Spain, Germany, France
Talc	9.490.000	China, USA, Korea

Source: United States Geological Survey (USGS)

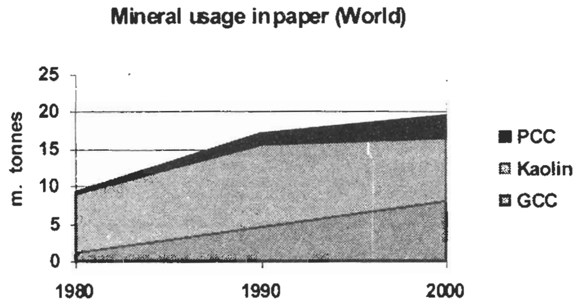
The principal industrial minerals are silica, ceramic (ball) clays, kaolin, calcium carbonate (chalk, limestone and marble), salt, talc, borates, feldspar, bauxite, potash (KCl), bentonite, phosphates, ... They also include some much less common minerals like andalusite, garnet, spodumene, kieserite, vermiculite, ... The main applications for these minerals are: glass, ceramics and refractory materials, paper, fertiliser, plastics, chemical industry, drugs and cosmetics, construction materials, paints, drilling muds, ...

While industrial minerals are found in an impressive amount of daily life products, the minerals industry is relatively poorly known from the general public. It is however by no means a small scale industry. The Industrial Minerals Association (IMA-Europe can be found on www.ima-eu.org) launched an awareness campaign in mid-2002 in order to generate more interest in this essential industry and to create a positive image in the public opinion.

The industrial minerals sector is mainly composed of small and medium-sized enterprises, but also includes some of the world's leading international companies. The large multinationals involved in non-metallic minerals production generate typically annual turnover in excess of €2bn and employ thousands of people. Some of the largest groups own over 150 production sites and quarries across the world. Interestingly it is an industry with a strong European base, and for example out of the top five largest industrial minerals producers in the world, four have their roots and headquarters in Europe. According to figures from IMA-Europe, members of this association operate more than 350 mines and quarries and 250 plants throughout Europe. They offer direct employment to some 40,000 people and process an annual volume of about 80m tonnes of non-metallic, non-fuel minerals, contributing a value of around €5bn to Europe's gross domestic product.

2. Minerals as functional fillers and pigments

The use of minerals as fillers in paper, paints and plastics has significantly evolved in the last two decades. This evolution took place in both quantitative (*see chart below*) and qualitative terms. The European paper industry alone has seen its minerals consumption increase from less than 4m tonnes to over 10m. tonnes in the last 20 years. From inert fillers used to reduce raw material costs, they have now become real functional additives. In some cases, minerals are no additives but raw materials – nearly 50% calcium carbonate for example in certain glossy high quality magazine paper or in breathable plastic films. Minerals improve a number of properties of the end product and are usually essential. One could say, for example, that minerals have allowed plastics to be so successful and displace more traditional materials in many applications of our daily life (automotive applications, plastics pipes and windows, ...). Minerals have clearly helped plastics to optimise their price/performance ratio.



Source: Calcium Carbonate – From the Cretaceous Period into the 21st Century, Birkhäuser Verlag

Today the principal mineral filler is natural calcium carbonate (calcite), also called Ground Calcium Carbonate (GCC). It is an ubiquitous mineral, which is exploited all over the world, and used in all mineral fillers applications: paper, paints and plastics. Precipitated calcium carbonate (PCC) and kaolin are also used in vast quantities, but their use as a filler is more restricted to paper.

In paper, minerals are used as fillers (entering the pulp before the web is formed) but more importantly as the main constituent of the coating formula, applied to the dry paper surface for further upgrading (glossy magazine or brochure paper for example).

In paints and coatings, minerals are dispersed in the binder and constitute the skeleton of the coating film. They increase the density and hardness of the film and reduce its permeability. They also provide the opacification of the film and regulate the level of gloss. Today a standard interior water-based (emulsion) paint may contain up to 70% of calcium carbonate.

3. Minerals in Plastics

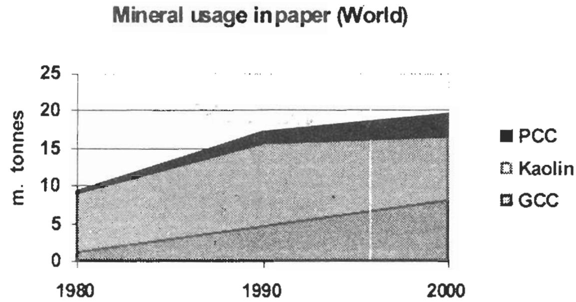
3.1. Introduction

Minerals are used in plastics for two main reasons:

1. To improve the processing behaviour and modifiy certain properties in the finished part

2. To achieve material costs reduction

While a large range of minerals are used in plastics, a handful of minerals account for most of the mineral usage in plastics: calcium carbonate, talc, kaolin, wollastonite and mica. Calcium carbonate can be used for the two above reasons, while the other minerals are only used for their ability to improve the properties of plastics.



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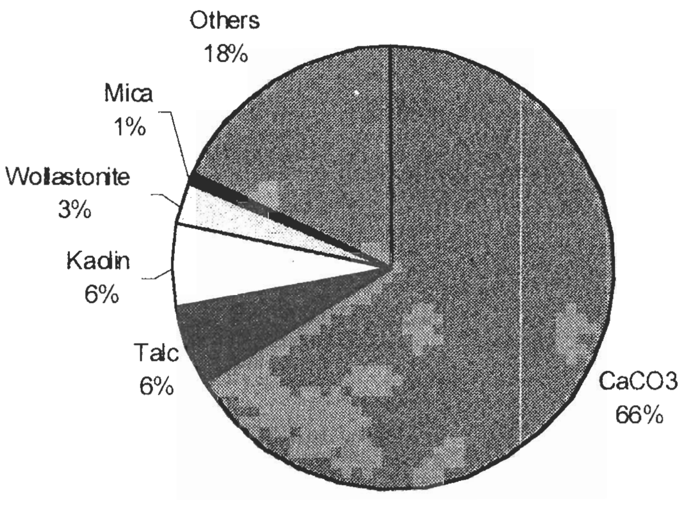
3.2. History of mineral usage in plastics

Although, there has been strong growth in the use of minerals in plastics over the last 30 years, there is nothing new about using minerals as fillers and extenders. Chalk mixed with linseed oil was used by medieval painters already. However, it is not until the 19th century that chalk started to be used industrially as a constituent of glazing putty (used for sealing windows). In this application, chalk was mixed with linseed oil. Since the beginning of the 20th century, chalk has been used as a filler in rubber goods and show soles. But it is really after the Second World War that mineral usage in plastics developed significantly. This development occurred of course in parallel to the development of plastics products, in particular PVC cables and pipes.

3.3. Market data

The plastics industry consumed about 11m tonnes of minerals in 2001. Calcium carbonate was by far the most important mineral accounting for nearly 70% of the consumption. Minerals are incorporated into a wide range of polymers, but over 90% of the minerals used in plastics go into polyvinyl chloride (PVC), polyethylene (PE), polypropylene (PP), rubber and unsaturated polyester.

World Plastics Filler Consumption 2001



Source: Industrial Minerals, November 2002

3.4. Effect of mineral additives on plastics properties

Minerals modify plastic product properties in the following way:

- Increase the Young's modulus (increase the rigidity of the plastic)
- Increase or decrease the impact resistance, depending on the form of the particles and their adhesion to the polymer matrix.
- Increase the surface hardness and the surface aspect of the finished parts
- Increase the density (important for noise attenuation properties and X-ray shielding)
- Improve the heat deflection temperature
- Reduce the shrinkage

But minerals have also an important influence on the processing of the plastic products:

- Faster heating and faster cooling: due to their significantly higher thermal conductivity.
- Improved homogenisation of the polymer melt and acts as a processing aid
- Better calibration of extruded profile (reduces surface tension and die swell)

The physico-chemical properties of minerals will influence how plastics properties are modified.

3.5. Mineralogical properties and influence on plastics

Most of the modifications caused by mineral additives to a polymer are controlled by three factors:

- Particle shape
- Particle size distribution
- Surface energy

Other important minerals properties include:

- Hardness
- Density
- Colour
- Level of impurities

3.5.1. Particle shape

When it comes to applications in plastics, particle shape is certainly the most important intrinsic property of the mineral. Unlike particle size, it is not a property which can be modified by processing.

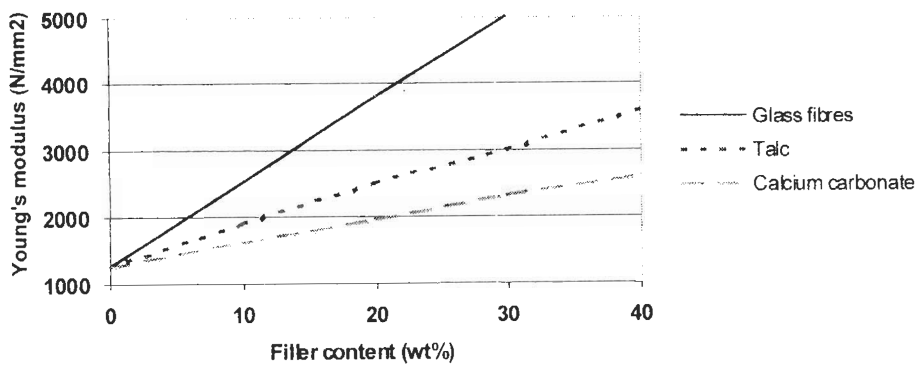
At a given filler loading, particle shape is of the greatest importance in determining the mechanical properties of the plastic product. Particle shape is usually measured by a dimensionless parameter, the aspect ration – the ratio between average diameter and average thickness of a particle. The higher the aspect ratio of the mineral, the higher the reinforcing effect on the polymer will be.

Particle shape of fillers and reinforcing agents

Shape	Sphere	Cube	Cuboid	Platelet	Fibre
Aspect ratio	1	~ 1	1,4-4	5-10	>10
Examples	Glass spheres, silicate microspheres	Calcium carbonate	Silica, barytes	Mica, talc, kaolin, graphite, aluminium trihydrate	Glass fibres, wollastonite

Source: Omya AG, Technical Information Plastics

Effect of aspect ratio on the stiffness of polypropylene



3.5.2. Particle size distribution

The particle size distribution (PSD) of a filler is usually given as a cumulative curve, indicating the amount per volume or weight of particles (%), which are smaller than a given size. In most cases the PSD of a filler can be described statistically by using the log normal distribution. In practice the filler manufacturer provides data indicating the average particle size (d50) and the top cut (eg. d98) – the sizes of which 50% and 98% of particles respectively are below. Particle size distribution is adjustable via grinding and classification. Most calcium carbonate fillers used in plastics have d50s in the range of 0,8μ to 5μ.

A precise top cut is of the utmost importance. The coarsest particles act as points of greatest stress concentration, where the crack or fracture occurs under load. Impact strength is significantly improved by using finer fillers, for example reducing the top cut of calcium carbonate from 25μ to 5μ leads to an increase in notched impact strength of 125% in a rigid PVC cable duct (containing 20% of filler).

3.5.3. Specific surface area

The specific surface area – expressed in m^2/g – is an extremely important physical parameter. The measurement can be made either by liquid nitrogen adsorption (BET method) or by permeability of air (Blair method). It is a measure of how many points of bonding are theoretically possible between the polymer chains and the additive material. In general most mechanical properties of a filled polymer will increase as the specific surface area increases.

However there is a limit to this and a higher specific surface area will also mean a greater proportion of fines, and as filler particles become smaller they show an increased tendency to agglomerate. Particles with a mean statistical particle diameter of 1 μ are held together by van der Waals forces ten million times more strongly than they are separated by gravitational forces. Once filler aggregates have formed, they can be difficult to disperse while mixed with the polymer.

3.5.4. Surface energy

The surface energy of a material (expressed in mJ/m^2) describes the energy that must be applied to increase the surface area of the solid by one square metre. In order to achieve optimal mechanical and optical properties in the end product, it is very important that all mineral particles are well dispersed in the polymer matrix. This is best achieved by matching the surface properties to the matrix into which dispersion is to take place. Polymers have surface energies which are much lower than minerals (200 mJ/m^2 for uncoated calcium carbonate against 15-50 mJ/m^2 for most common polymers). By coating the surface of calcium carbonate with stearic acid, surface energy can be reduced to 40 mJ/m^2, corresponding to the surface energy of PVC. In addition, surface coating reduces the adsorption of stabilisers and lubricants at the filler surface. This contributes to the much better heat stability of coated calcium carbonate.

3.5.5. Hardness

The Moh's hardness of minerals greatly influences its ability to lead to wear of the processing machinery. It is however not the only deciding factor. Abrasion of machinery also depends on particle shape, particle size and filler concentration.

3.5.6. Thermal conductivity

Another important property of minerals is their thermal conductivity, which is significantly higher than that of polymers (*see table*). The specific heat of minerals, on the other hand, is only half as much as that of polymers. The heat introduced and generated during processing of plastics is transmitted through the mixture more quickly. The heat is also conducted away faster during cooling. Thus in the case of injection moulding for example, the cycle time can be reduced, resulting in increased throughput.

Thermal conductivity

Material	Thermal conductivity ($Wm^{-1}K^{-1}$)
HDPE	0,45
PP	0,20
$CaCO_3$	2,70
PP + 20% $CaCO_3$	0,42
PP + 40% $CaCO_3$	0,56

3.6. Main minerals used in plastics: properties and applications

3.6.1. Calcium carbonate

As already mentioned ground calcium carbonate in its uncoated or coated forms is the most important mineral for the plastics industry. Calcium carbonate has a relatively low Moh's hardness (3), which means abrasion of tools and extrusion screws is limited. It has a high chemical purity and high degree of whiteness. It is non toxic and tasteless making it suitable for food packaging applications.

At the low end of the quality spectrum is the flooring industry, where relatively coarse calcium carbonate is used as a cheap filler in carpet backing or in vinyl and rubber flooring.

The most important type of polymer containing calcium carbonate is PVC. Calcium carbonate is used as a low cost filler in PVC cables for low voltage applications. In PVC pipes and profiles (eg. for windows), calcium carbonate is a functional filler. It is used to reduce formulation costs but also to improve processing and calibration of the extruded products. For such applications fine to ultra-fine treated calcium carbonate are usually recommended.

But calcium carbonate is also used extensively in polyolefines, for example as part of anti-blocking masterbatches, or to improve the stiffness and reduce cooling time of many extruded and injection moulded parts made of polyethylene and polypropylene. Calcium carbonate is widely used in unsaturated polyester finding applications in the automotive industry for example.

In breathable film, calcium carbonate allows the film to breath thanks to a network of micropores and imparts a number of other vital properties. This type of microporous film is stretched tearing the polymer chains away from the surface of the calcium carbonate particles. This produces micropores in the film cross-section which allow the passage of water vapour during use. Applications for this type of film, which typically contains 50% calcium carbonate, are in baby diapers and feminine hygiene products as well as under-roof sheets for buildings.

3.6.2. Talc

Talc is lamellar mineral which because of its shape is able to increase stiffness of plastics significantly. It has also a very low Moh's hardness – in fact it has the lowest of all mineral: 1. Most commercial talcs for the plastics industry have a mean particle size of 1 to 15µm. By far the most important type of polymer containing talc is polypropylene (PP). Compounds or granulates of PP mixed with talc are used by many processors of PP to increase stiffness or to improve mechanical properties at high temperature. These injection moulded or extruded parts find uses in automotive applications and electrical appliances, as well as in many other areas.

3.6.3. Kaolin

Kaolin is a hydrated aluminium silicate that is produced by the weathering of granite. Grades suitable for plastics are found in Cornwall as well as in the Georgian kaolin belt of North America. Water washed kaolin is widely used as a reinforcing filler in the rubber industry, where it provides higher tear strength and tensile strength. Kaolin can be calcined at temperatures ranging from 750°C to 1100°C. This type of kaolin is used in PVC cables to improve the electrical resistivity.

3.6.4. Wollastonite

Due to its needle shape, this calcium silicate provides significant improvement in stiffness and flexural strength. It also imparts a higher heat distortion temperature. Wollastonite finds uses in technical and specialist applications for PP, polyamides and unsaturated polyesters. It can often replace partly fibre glass.

3.6.5. Mica

The term mica covers a wide range of aluminium silicates. All micas feature perfect cleavage and have a monoclinic crystal system. Mica acts as a reinforcing agent in epoxy and phenolic resins as well as in PP. Some special grades (often surface modified) are used as metallic effect pigments.

3.6.6. Other minerals

There are many other minerals or mineral-derived additives and pigments used in the plastics industry. Barytes are used in special applications where sound absorption in needed (soil water pipes for hotels or apartment blocks for examples) or in X-ray shielding (medical applications) replacing lead based materials. TiO_2 derived from ilmenite or rutile is the leading white pigment in the plastics industry. Flame retardants additives include many minerals such as brucite (natural MgOH), synthetic MgOH, and aluminium hydroxide (produced from bauxite).

3.7. Conclusions

Minerals play and will continue to play a significant role in the plastics industry. Most plastics used in our daily lives are actually composites made up of polymers and natural minerals. By improving many properties of plastics and making them more cost effective, it can be clearly stated that they have helped plastics reach the high level of market penetration they enjoy today in comparison to metals, wood, ceramics and other materials.

4. Source of information

Omya AG, "Technical Information Plastics"

Calcium Carbonate – From the Cretaceous Period into the 21st Century, edited by F. Wolfgang Tegethoff, published by Birkhäuser Verlag, CH-4010 Basel

Industrial Minerals Information Ltd, Various articles and publications

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