

Fancy fillers

Fillers are no longer just added to polymers to reduce costs, but are increasingly enhancing properties of the compound. Calcium carbonate, talc, clay, mica, wollastonite and glass fibre are all widely used in polymer compounding operations. However, there are some lesser well known fillers that can provide some useful properties in polymers. Dr. Chris DeArmitt and Professor Roger Rotheron explain.

Fillers have long been used to modify the properties of polymers, including fibres, coatings, sealants and adhesives. To many people, the word filler is associated with

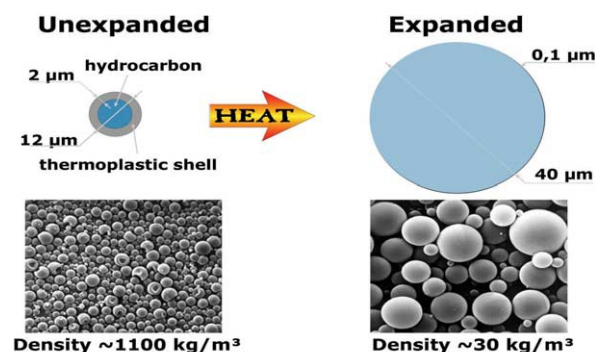
cost reduction, but in recent years it has become more widely recognized that fillers alter all properties of the material in which they are mixed. This means that even when

the main goal is cost reduction, one must understand the effects of adding fillers in terms of altered processing and final properties. Similarly, when the primary aim is to enhance properties, one must also understand the effects of the filler, both positive and otherwise. Previous articles in *Plastics Additives & Compounding* have shown how fillers can be used effectively to alter polymer properties. Using fillers can allow a performance/cost ratio not found for unfilled polymers, or in other instances, the filler imparts properties not possible in unfilled polymers. Most commonly, fillers are used to assist processing and to upgrade the mechanical properties of the host polymer. Several well-known fillers are used in that capacity; such as calcium carbonate, talc, clay, mica, wollastonite and glass fibre. Additionally, there are many other fillers that are used, not to change mechanical properties, but rather to impart some other property such as conductivity (electrical or thermal), sound and vibration damping, density changes, magnetism, reduced warpage and so on. This article introduces some of these less well-known fillers.

Expandable microspheres

Most fillers are minerals and as such they are inorganic and relatively inert. For example, they maintain their shape both during processing and afterwards. In sharp contrast, expandable microspheres are organic and change their shape during processing. The particles are composed of a polymeric shell, which contains an innocuous hydrocarbon liquid. As these beads are heated, the shell softens and the

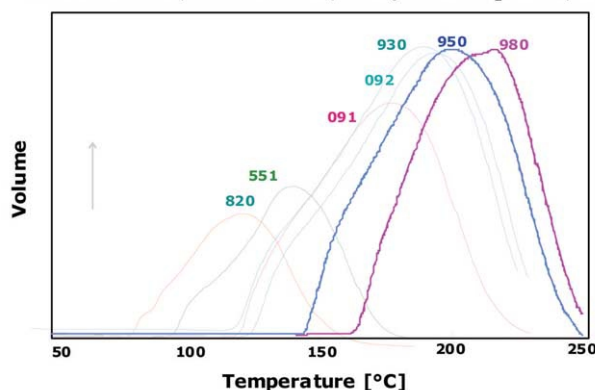
Thermoexpandable Microspheres



A.Kron, Expancel, 2005-03-09

Figure 1: Expancel expansion schematic.

Volume as a function of temperature when heating [20°C/min] various thermoexpandable microsphere grades in N₂-atmosphere



A. Kron, Expancel, 2005-06-26

Figure 2: Tunable expansion temperature.

trapped liquid boils, the pressure from the trapped vapour forces the particles to expand to many times their original volume. By tuning the chemical composition of the polymeric shell and the boiling point of the liquid, one can tune the expansion temperature range of the particles over a wide range.

Such particles find uses in diverse applications, including polymers, paper board and printing ink. One application is in printing paper for Braille books. By adding the particles to the paper it becomes thermally sensitive. When such paper is used with a thermal printer, the heat from the printer causes the particles to expand only in specified locations, *i.e.*: where the paper is heated by the printing head. This causes elevated dots on the paper that can be read by visually impaired people.

In polymers, these particles can be expanded during processing and then as the polymer cools the bubbles created are locked into the polymer to give a material with lowered density, *i.e.*: for flotation aids and in filled thermosets, a material with increased stress relaxing ability. In paper board, additional bulk is achieved by the use of low temperature expanding microspheres added to the pulp.

Diatomaceous Earth

Diatomaceous Earth has long been used as an anti-block for polymer films. The particles impart a microscopic roughness to the film and the refractive index of the filler



Figure 3: Diatomaceous Earth from freshwater deposit in Mexico [Micrograph courtesy of World Minerals]



Figure 4: Diatomaceous Earth with one predominant type of Diatom [Micrograph courtesy of World Minerals]

Table 1: Diatomaceous Earth in Nylon 6

[Courtesy of World Minerals]

Filler	Level % w/w	Tensile modulus /MPa	Flexural modulus /MPa	Tensile strength /MPa	Elongation at yield /%	Impact strength Un-notched /kJ/m ²
None	0	2750	1420	67	3.7	>100
Glass beads	35	5265	2640	58	2.5	22
Silane treated calcined clay	35	5700	2990	79	3.0	62
Untreated DE	30	4900	2445	70	3.0	36
Treated DE	30	4760	2465	72	3.7	>100

Fillers

(1.45) is close to that of many thermoplastics so transparency is maintained. More recently work has been done to develop this mineral as a filler, particularly in nylons and in rubber. The particles are actually the skeletal remains of sea algae and are composed of silica and so the specific shape can vary widely depending upon the prevalent type of diatom where the deposit was laid down.

In order to develop the Diatomaceous Earth (DE) as a filler, work was done to classify the product to give an appropriate size distribution and also to identify the optimal surface treatment for the DE in each matrix material. The results below show the properties given by DE in nylon 6 as compared to those from other common fillers for that polymer. The surface treatment aids wetting of the

micro-voids in the DE by the polymer melt, giving rise to the improved impact resistance of the treated DE over that of the untreated grade.

Magnetite

Most mineral fillers have a density in the range 2.5-3 g/cm³ whereas polymers lie in the range 0.9-1.4 g/cm³, therefore fillers usually lead to increased density. Added density leads to added transportation costs and in many applications is viewed as an unwelcome side effect of adding mineral fillers to polymers.

However, there are some instances where it is favourable to increase density. For example, it is well-known that sound deadening can be accomplished by using dense materials. Such formulations are composed of a dense filler in a soft, gummy polymer (such as EVA, PVB, bitumen).

Barium sulphate (density of 4.48 g/cm³) is by far the most well-known dense filler for such applications. In recent years magnetite, Fe₃O₄ (density of 5.1 g/cm³) has been introduced into the market and gained acceptance in automotive and other applications. It has an interesting combination of properties. Firstly, the high density makes it useful, but it also has some electrical and thermal conductivity, which can be useful for electric motor housings. The thermal conductivity aids in heat dissipation and the electrical conductivity contributes to electromagnetic shielding. There are some potential drawbacks though. The relatively high hardness (Mohs' 5.5-6) could lead to undesirably rapid wear on processing equipment, but this has not been reported to be a problem, probably because machine wear depends on other factors like particle size and shape, not hardness alone.

Additionally, the high iron content might be a concern as it is well documented that transition metals like iron can lead to rapid polymer degradation, especially in polyolefins like PE and PP. In reality it turns out that the magnetite does not cause big stability problems as the chemical form of the iron is far more important than the amount.



Figures 5 and 6: Magnetite is becoming increasingly used as filler in automotive applications. [Photographs courtesy of Minelco]

Beta Spodumene - Lithium Feldspar, $\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$

There is a specialized market in very low thermal expansion fillers. Beta Spodumene is one such product. It is produced from the naturally occurring mineral Spodumene. Upon heating to 1082°C, Spodumene undergoes a phase transition and expands going from a density of 3.2 g/cm³ for Spodumene to 2.4 g/cm³ for the Beta Spodumene. The Beta Spodumene is notable for having an exceptionally low coefficient of thermal expansion, $\sim 1 \times 10^{-6}/^\circ\text{C}$ over the range 25-1000°C. This property has been used for ceramic oven-to-table ware as the material is resistant to thermal shock due

to the low coefficient of thermal expansion. Minerals are often added to polymers to reduce the coefficient of thermal expansion. Polymers typically have values in the range $\sim 10 \times 10^{-5}$ mm.mm⁻¹ °C⁻¹ whereas many minerals are a factor of ten lower $\sim 10 \times 10^{-6}$ mm.mm⁻¹ °C⁻¹. The use of mineral fillers greatly reduces the coefficient of thermal expansion according to the linear law of mixtures in proportion to the volume percentage of polymer replaced by mineral. For applications demanding exceptionally low thermal expansion, Beta Spodumene may be used.

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