



GELCLAD

Highly efficient cladding
eco-panels with improved
nano-insulation properties

DELIVERABLE D2.1

Gelclad functional
fillers and
thermoplastics

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Abstract

This deliverable provides a review of suitable functional fillers for common thermoplastics. Focus are fillers and thermoplastics with a big market. Building and construction form a large part of the global economy and this industry showed a growth rate of 1.8% worldwide in 2001. Thermoplastic polymer materials have been steadily replacing traditional materials in this sector. Construction applications of plastics include pipes and guttering, window and door profiles, glazing, roofing, sealants and adhesives, cement, insulation, flooring and building panels. Civil engineering applications include geomembranes, road and sports surfaces, building reinforcement and bridge building. This is a critical market for plastics.

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SUMMARY

The overall objective of the GELCLAD project is to develop a novel highly affordable and efficient smart cladding eco-panel solution, possessing excellent thermal insulation performance (low thermal conductivity) by integrating. This deliverable provides a review of suitable functional fillers for common thermoplastics. It focuses on fillers and thermoplastics with a big market.

2

THERMOPLASTICS

A thermoplastic, or thermosoftening plastic, is a plastic material, a polymer, that becomes pliable or moldable above a specific temperature and solidifies upon cooling (1) (2).

Most thermoplastics have a high molecular weight. The polymer chains associate through intermolecular forces, which weaken rapidly with increased temperature, yielding a viscous liquid. Thus, thermoplastics may be reshaped by heating and are typically used to produce parts by various polymer processing techniques such as injection molding, compression molding, calendaring, and extrusion (3)(4). Thermoplastics differ from thermosetting polymers, which form irreversible chemical bonds during the curing process. Thermosets do not melt, but decompose and do not reform upon cooling.

Above its glass transition temperature and below its melting point, the physical properties of a thermoplastic change drastically without an associated phase change. Some thermoplastics do not fully crystallize below the glass transition temperature, retaining some or all of their amorphous characteristics. Amorphous and semi-amorphous plastics are used when high optical clarity is necessary, as light is scattered strongly by crystallites larger than its wavelength. Amorphous and semi-amorphous plastics are less resistant to chemical attack and environmental stress cracking because they lack a crystalline structure.

Brittleness can be decreased with the addition of plasticizers, which increases the mobility of amorphous chain segments to effectively lower the glass transition temperature. Modification of the polymer through copolymerization or through the addition of non-reactive side chains to monomers before polymerization can also lower it. Before these techniques were employed, plastic automobile parts would often crack when exposed to cold temperatures. These are linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling.

Building and construction form a large part of the global economy and this industry showed a growth rate of 1.8% worldwide in 2001. Thermoplastic polymer materials have been steadily replacing traditional materials in this sector. Construction applications of plastics include pipes and guttering, window and door profiles, glazing, roofing, sealants and adhesives, cement, insulation, flooring and building panels. Civil engineering applications include geomembranes, road and sports surfaces, building reinforcement and bridge building. This is a critical market for plastics. The most important thermoplastic polymer materials are described in the following.

2.1. HDPE

HDPE is used for many packaging applications because it provides excellent moisture barrier properties and chemical resistance. However, HDPE, like all types of polyethylene, is limited to those food packaging applications that do not require an oxygen or CO₂ barrier. In film form, HDPE is used in snack food packages and cereal box liners; in blow-molded bottle form, for milk and non-carbonated beverage bottles; and in injection-molded tub form, for packaging margarine, whipped toppings and deli foods. Because HDPE has good chemical resistance, it is used for packaging, many household products, as well as industrial chemicals such as detergents, bleach and acids. General uses of HDPE include injection-molded beverage cases, bread trays as well as films for grocery sacks and bottles for beverages and household chemicals (12).



Figure 1: Thermoplastic polyethylene

Around 1.85 million tons of high density polyethylene are used annually in construction, amounting to roughly 10% of total global consumption.

2.2. LDPE

LDPE is predominantly used in film applications due to its toughness, flexibility and transparency. LDPE has a low melting point making it popular for use in applications where heat sealing is necessary. Typically, LDPE is used to manufacture flexible films such as those used for dry cleaned garment bags and produce bags. LDPE is also used to manufacture some flexible lids and bottles, and it is widely used in wire and cable applications for its stable electrical properties and processing characteristics (12).

2.3. PP

PP has excellent chemical resistance and is commonly used in packaging. It has a high melting point, making it ideal for hot fill liquids. PP is found in everything from flexible and rigid packaging to fibers for fabrics and carpets and large molded parts for automotive and consumer products. Like other plastics, polypropylene has excellent resistance to water and to salt and acid solutions that are destructive to metals. Typical applications include ketchup bottles, yoghurt containers, medicine bottles, pancake syrup bottles and automobile battery casings (12). Low density polyethylene and polypropylene are also used extensively in the construction sector.

2.4. PS

Polystyrene (PS) is a synthetic aromatic polymer made from the monomer styrene. Polystyrene can be solid or foamed. General-purpose polystyrene is clear, hard, and rather brittle. It is an inexpensive resin per unit weight. It is a rather poor barrier to oxygen and water vapor and has a relatively low melting point. Polystyrene is one of the most widely used plastics, the scale of its production being several million tonnes per year. Polystyrene can be naturally transparent, but can be coloured with colorants. Uses include protective packaging (such as packing peanuts and CD and DVD cases), containers (such as "clamshells"), lids, bottles, trays, tumblers, and disposable cutlery.

As a thermoplastic polymer, polystyrene is in a solid (glassy) state at room temperature but flows if heated above about 100 °C, its glass transition temperature. It becomes rigid again when cooled. This temperature behaviour is exploited for extrusion (as in Styrofoam) and also for molding and vacuum forming, since it can be cast into molds with fine detail. Polystyrene is very slow to biodegrade and is, therefore, a focus of controversy among environmentalists. It is increasingly abundant as a form of litter in the outdoor environment, particularly along shores and waterways, especially in its foam form, and also in increasing quantities in the Pacific Ocean (13).

Polystyrene is also used extensively, primarily in insulation applications.

2.5. ABS

Acrylonitrile butadiene styrene (ABS) (chemical formula $(C_8H_8)_x(C_4H_6)_y(C_3H_3N)_z$) is a common thermoplastic polymer. Its glass transition temperature is approximately 105 °C (221 °F). ABS is amorphous and therefore has no true melting point.

ABS is a terpolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. The proportions can vary from 15 to 35% acrylonitrile, 5 to 30% butadiene and 40 to 60% styrene. The result is a long chain of polybutadiene criss-crossed with shorter chains of poly(styrene-co-acrylonitrile). The nitrile groups from neighbouring chains, being polar, attract each other and bind the chains together, making ABS stronger than pure polystyrene. The styrene gives the plastic a shiny, impervious surface. The polybutadiene, a rubbery substance, provides toughness even at low temperatures. For the majority of applications, ABS can be used between -20 and 80 °C (-4 and 176 °F) as its mechanical properties vary with temperature. The properties are created by rubber toughening, where fine particles of elastomer are distributed throughout the rigid matrix.

2.6. PVC

PVC has excellent transparency, chemical resistance, long term stability, good weatherability and stable electrical properties. Vinyl products can be broadly divided into rigid and flexible materials. Rigid applications are concentrated in construction markets, which include pipe and fittings, siding, rigid flooring and windows. PVC's success in pipe and fittings can be attributed to its resistance to most chemicals, imperviousness to attack by bacteria or microorganisms, corrosion resistance and strength. Flexible vinyl is used in wire and cable sheathing, insulation, film and sheet, flexible floor coverings, synthetic leather products, coatings, blood bags, and

medical tubing. In near future PVC will not be fittable from the environmental view because it produces the toxic gases during burning. PVC or Poly Vinyl Chloride is a regular, lightweight but strong plastic used in construction industry. It is made softer by adding plasticizers. Rigid PVC or Vinyl siding refers to PVC in which plasticizers are not added. The following diagram shows the use of PVC especially in the construction sector.

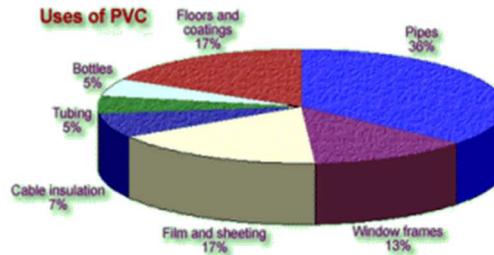


Figure 2: Uses of PVC, <http://www.lenntech.com/polyvinyl-chloride-pvc.htm>

PVC has been widely used for multiple functions in the construction industry for over half a century. Its durability, versatility and strong but lightweight nature have resulted in it being used for the following applications.

- **Pipes:** PVC pipes have been used since last 60 years. In comparison to traditional pipe material, PVC provides energy saving service, cost effective distribution and a maintenance free, safe, lifetime of service. PVC pipes do not contribute to the degradation of the environment and suffer fewer leaks or breakages than other material. PVC pipes are used for water, drainage and waste carrying because buried pipes are expected to last over 100 years.
- **Windows:** PVC based windows have been fabricated since 1960's. Since the past 15 years, 85% of new and replacement projects of windows have been using PVC in the U.K. PVC windows are durable and tough with an average life span exceeding 35 years.
- **Flooring:** Over last 50 years, vinyl flooring has been in use extensively for flooring in both private and public buildings whether small or large. The main benefits of PVC flooring are: They are durable, are available in a variety of patterns and colours, easily installed, easy to clean, of variable thickness and easily recyclable. PVC flooring is widely used in hotels, hospitals and homes all over the world.
- **Roofing:** PVC roofing that is reinforced is simple to install, has low maintenance cost and lasts over 30 years. It can be used to create web-like ultra-lightweight structures. Tensile PVC fabric is used for high profile, 'signature' projects.
- **Inflatable structures:** Inflatable, large structures can be made with PVC which is flexible and strong
- **Light structures:** With modern PVC architecture, web like structures can be constructed within limited constraints. Being light, they hold their ground and have reduced impact on the environment.

These are some of the uses of PVC in the construction sector. To get high-quality PVC, contact PVC sheet manufacturers in Delhi. PVC is emerging as the most versatile material in the construction sector.

2.7. PLA

Poly(lactic acid) or polylactic acid or polylactide (PLA) is a biodegradable and bioactive thermoplastic aliphatic polyester derived from renewable resources, such as corn starch (in the United States and Canada), cassava roots, chips or starch (mostly in Asia), or sugarcane (in the rest of the world). In 2010, PLA had the second highest consumption volume of any bioplastic of the world. The name "polylactic acid" does not comply with IUPAC standard nomenclature, and is potentially ambiguous or confusing, because PLA is not a polyacid (polyelectrolyte), but rather a polyester. PLA can be processed by extrusion such as 3d printing, injection molding, film and sheet casting, and spinning, providing access to a wide range of materials.

PLA is used as a feedstock material in desktop fused filament fabrication 3D printers (e.g. RepRap). PLA printed solids can be encased in plaster-like moulding materials, then burned out in a furnace, so that the resulting void can be filled with molten metal. This is known as "lost PLA casting", a type of investment casting.

Being able to degrade into innocuous lactic acid, PLA is used as medical implants in the form of anchors, screws, plates, pins, rods, and as a mesh. Depending on the exact type used, it breaks down inside the body within 6 months to 2 years. This gradual degradation is desirable for a support structure, because it gradually transfers the load to the body (e.g. the bone) as that area heals. The strength characteristics of PLA and PLLA implants are well documented.

PLA can also be used as a decomposable packaging material, either cast, injection-molded, or spun. Cups and bags have been made from this material. In the form of a film, it shrinks upon heating, allowing it to be used in shrink tunnels. It is useful for producing loose-fill packaging, compost bags, food packaging, and disposable tableware. In the form of fibers and nonwoven fabrics, PLA also has many potential uses, for example as upholstery, disposable garments, awnings, feminine hygiene products, and diapers.

Racemic and regular PLLA has a low glass transition temperature, which is undesirable. A stereocomplex of PDLA and PLLA has a higher glass transition temperature, lending it more mechanical strength. It has a wide range of applications, such as woven shirts (ironability), microwavable trays, hot-fill applications and even engineering plastics (in this case, the stereocomplex is blended with a rubber-like polymer such as ABS). Such blends also have good form stability and visual transparency, making them useful for low-end packaging applications. Pure poly-L-lactic acid (PLLA), on the other hand, is the main ingredient in Sculptra, a long-lasting facial volume enhancer, primarily used for lipoatrophy of cheeks. Progress in biotechnology has resulted in the development of commercial production of the D enantiomer form, something that was not possible until recently. Currently, the SPI resin identification code 7 ("others") is applicable for PLA. In Belgium, Galactec started the first pilot unit to chemically recycle PLA (Loopla). Unlike mechanical recycling, waste material can hold various contaminants. Polylactic acid can be recycled to monomer by thermal depolymerization or hydrolysis. When purified, the monomer can be used for the manufacturing of virgin PLA with no loss of original properties (cradle-to-cradle recycling).

Amycolatopsis and Saccharotrix are able to degrade PLA. A purified protease from Amycolatopsis sp., PLA depolymerase, can also degrade PLA. Enzymes such as pronase and most effectively proteinase K from Tritirachium album degrade PLA.

Pure PLLA foams undergo selective hydrolysis when placed in an environment of Dulbecco's modified Eagle's medium (DMEM) supplemented with fetal bovine serum (FBS) (a solution mimicking body fluid). After 30 days of submersion in DMEM+FBS, a PLLA scaffold lost about 20% of its weight.

The German company JELU (5) has developed a fully compostable biocomposite for industrial processing. The new material made from polylactides (PLA) and wood fibres is a wood plastic composite (WPC), which can be recycled in composting plants. It is suitable for injection moulding and extrusion on conventional plastics processing machines. Wood plastic composite combines the properties of both wood and plastics: the products are mouldable like plastics and firm like wood. JELU compounds PLA with wood fibres to form a homogeneous material that consists of 100% renewable resources. In its basic blend, the compound contains 40% PLA and 60% wood fibres. The material is granulated, as the processing of granulates makes it possible to create extremely homogeneous end products. WPC granulate from JELU has consistent running properties on the machine, facilitating a higher output. Compounding also gives the biocomposite a higher density, improving the properties of the material. As a result, products have greater strength and stiffness. PLA-WF 30 % from GEHR is a composite material of polylactide, a small amount of a petroleum-based polyester and wood fibers (30%). It possesses high mechanical strength thanks to the excellent binding of the wood fibers and the polymer blend. This is comparable with standard fiber-reinforced polymers. It also displays good thermal insulation and conforms to the standards governing toys. (6)

A PLA based material was used in the construction sector for developing the bioplastic facade mock-up.



Figure 3: Bioplastic facade mock-up

The bioplastic facade mock-up was created within the framework of Research Project Bioplastic Facade, a project supported by EFRE (European Fund for Regional Development). It demonstrates one of the possible architectonic and constructional applications of the bioplastic materials developed in the course of this project. The blueprint is based on a triangular net made up of mesh elements of varying sizes. Collaborating material scientists (Tecnaro), architects (ITKE), product designers (spek Design), manufacturing technicians (Bauer), and environmental experts (ISWA) were able to develop a new material for facade cladding which is thermoformable and made primarily (>90%) from renewable resources. ARBOBLEND[®], a special type of bioplastic granules, can be extruded into sheets which are further processable as

needed: They can be drilled, printed, laminated, laser cut, CNC-milled, or thermoformed to achieve different surface qualities and structures and various moulded components can be produced. The semi-finished products serve as cladding for flat or free-formed interior and exterior walls. The material can be recycled and meets the high durability and inflammability standards for building materials. The goal of the project was to develop a maximally sustainable yet durable building material while keeping petroleum-based components and additives to a minimum. The ecological audit was completed by project partner ISWA (Institute for water engineering, water quality, and waste management). Furthermore, the materials' resistance to microbial degradation was determined. This research project marks the first occasion for the development of bioplastic sheets that are made primarily of renewable resources, can be freely formed, and are furthermore designed for application in the building sector and specifically for building exteriors. At the beginning of this project, such a product was not available on the market. The conception of this material as flame-retardant sheet material also aims at applications for building interiors with this new development, we can therefore soon offer a product that addresses two trends:

- the increasing demand for resource-efficient and sustainable building materials
- the increasing development of buildings featuring double-curved geometries and planar facade components with 3D effects (relief)

Extruded sheets made of the bioplastic materials are thermoformed into identical pyramidal moulding components. The necessary process of contour milling allows for multiple variations among the moulding components as identical thermoformed parts can be processed differently using various CNC milling paths. This allows for the cladding of freeform areas with a single moulded component. The plastic waste that results from CNC milling process is regranulated and directly returned to the extruding process. At the end of their useful life, the facade sheets can be composted or disposed of almost carbon-neutrally.

The freeform bioplastic facade functions as a sheet material based shell structure with additional load-bearing and bracing ring carriers and joists. Contrary to common non-loadbearing facade constructions, this construction involves the load-bearing properties of the double curved skin (made of 3,5 mm thick bioplastic pyramids that are mechanically coupled) in the load-bearing and bracing processes of the entire system. On the one hand, this innovative measure shows the potential of modified bioplastics as a bracing material (up to $E \approx 4000 \text{ N/mm}^2$) suitable for exterior applications as it adds only a minor load due to its own weight (13 kN/m^3); on the other hand, it allows for the construction of a facade that utilizes a minimized number of points of support and/or mounting brackets on the structural work behind it.

Due to their mechanical weakness, the following polymers are less likely to be used in the construction sector:

2.8. PHB

Polyhydroxybutyrate (PHB) is a polyhydroxyalkanoate (PHA), a polymer belonging to the polyesters class that are of interest as bio-derived and biodegradable plastics. The poly-3-hydroxybutyrate (P3HB) form of PHB is probably the most common type of polyhydroxyalkanoate, but other polymers of this class are produced by a variety of organisms: these include poly-4-hydroxybutyrate (P4HB), polyhydroxyvalerate (PHV), polyhydroxyhexanoate (PHH), polyhydroxyoctanoate (PHO) and their copolymers.

Most commercial plastics are synthetic polymers derived from petrochemicals. They tend to resist biodegradation. PHB-derived plastics are attractive because they are compostable and derived from renewables and are bio-degradable.

ICI had developed the material to pilot plant stage in the 1980s, but interest faded when it became clear that the cost of material was too high, and its properties could not match those of polypropylene.

In 1996 Monsanto (who sold PHB as a copolymer with PHV under the trade name Biopol) bought all patents for making the polymer from ICI/Zeneca. However, Monsanto's rights to Biopol were sold to the American company Metabolix in 2001 and Monsanto's fermenters producing PHB from bacteria were closed down at the start of 2004. Monsanto began to focus on producing PHB from plants instead of bacteria. But now with so much media attention on GM crops, there has been little news of Monsanto's plans for PHB.

In June 2005, a US company, Metabolix, received the Presidential Green Chemistry Challenge Award (small business category) for their development and commercialisation of a cost-effective method for manufacturing PHAs in general, including PHB.

Biopol is currently used in the medical industry for internal suture. It is non-toxic and biodegradable, so it does not have to be removed after recovery. Firmicutes and proteobacteria can degrade PHB. *Bacillus*, *Pseudomonas* and *Streptomyces* species can degrade PHB. *Pseudomonas lemoigne*, *Comamonas* sp. *Acidovorax faecalis*, *Aspergillus fumigatus* and *Variovorax paradoxus* are soil microbes capable of degradation. *Alcaligenes faecalis*, *Pseudomonas*, and *Illyobacter delafieldi*, are obtained from anaerobic sludge. *Comamonas testosteroni* and *Pseudomonas stutzeri* were obtained from sea water. Few of these are capable of degrading at higher temperatures; notably excepting thermophilic *Streptomyces* sp. and a thermophilic strain of *Aspergillus* sp.

2.9. Thermoplastic starch

Thermoplastic starch currently represents the most widely used bioplastic, constituting about 50 percent of the bioplastics market. Simple starch bioplastic can be made at home. Pure starch is able to absorb humidity, and is thus a suitable material for the production of drug capsules by the pharmaceutical sector. Flexibiliser and plasticiser such as sorbitol and glycerine can also be added so the starch can also be processed thermoplastically. The characteristics of the resulting bioplastic (also called "thermo-plastical starch") can be tailored to specific needs by adjusting the amounts of these additives.

Starch-based bioplastics are often blended with biodegradable polyesters to produce starch / polycaprolactone or starch/Ecoflex (polybutylene

adipate-co-terephthalate produced by BASF). blends. These blends are used for industrial applications and are also compostable. Other producers, such as Roquette, have developed other starch/polyolefin blends. These blends are not biodegradable, but have a lower carbon footprint than petroleum-based plastics used for the same applications

2.10. Cellulose acetate

Cellulose acetate is the acetate ester of cellulose. It was first prepared in 1865. Cellulose acetate is used as a film base in photography, as a component in some coatings, and as a frame material for eyeglasses; it is also used as a synthetic fiber in the manufacture of cigarette filters and playing cards. In photographic film, cellulose acetate replaced nitrate film in the 1950s, being far less flammable and cheaper to produce.

Cellulose acetate and cellulose triacetate are mistakenly referred to as the same fiber; although they are similar, their chemical compositions and formulae differ. Triacetate is known as a generic description or primary acetate containing no hydroxyl group. Acetate fiber is known as modified or secondary acetate having two or more hydroxyl groups. Triacetate fibers, although no longer produced in the United States, contain a higher ratio of acetate-to-cellulose than do acetate fibers.

Cellulose acetate film was introduced in 1934 as a replacement for the cellulose nitrate film stock that had previously been standard. When exposed to heat or moisture, acids in the film base begin to deteriorate to an unusable state, releasing acetic acid with a characteristic vinegary smell, causing the process to be known as "vinegar syndrome." Acetate film stock is still used in some applications, such as camera negative for motion pictures. Since the 1980s, polyester film stock (sometimes referred to under Kodak's trade name "ESTAR Base") has become more commonplace, particularly for archival applications. Acetate film was also used as the base for magnetic tape, prior to the advent of polyester film.

Cellulose acetate magnetic tape was introduced by IBM in 1952 for use on their IBM 726 tape drive in the IBM 701 computer. It was much lighter and easier to handle than the metal tape introduced by UNIVAC in 1951 for use on their UNISERVO tape drive in the UNIVAC I computer. In 1956 cellulose acetate magnetic tape was replaced by the more stable PET film magnetic tape for use on their IBM 727 tape drive.

Cellulose acetate fiber is one of the earliest synthetic fibers and is based on cotton or tree pulp cellulose ("biopolymers"). These "cellulosic fibers" have been replaced in many applications by cheaper petrol-based fibers (nylon and polyester) in recent decades. Trade names for acetate include Acele, Avisco, Celanese, Chromspun and Estron.

Acetate shares many similarities with rayon, and was formerly considered as the same textile. Acetate differs from rayon in the employment of acetic acid in production. The two fabrics are now required to be listed distinctly on garment labels.

Rayon resists heat while acetate is prone to melting. Acetate must be laundered with care either by hand-washing or dry cleaning. Acetate garments will disintegrate when heated in a tumble dryer.

The breathable nature of the fabric suits it for use as a lining. Acetate fabric is used frequently in wedding gowns and other bridal attire. Its lustrous sheen and smooth, satiny texture make it a good synthetic alternative to silk.

The Federal Trade Commission definition for acetate fiber is "A manufactured fiber in which the fiber-forming substance is cellulose acetate. Where not less than 92 percent of the hydroxyl groups are

acetylated, the term triacetate may be used as a generic description of the fiber."

Acetate is derived from cellulose by deconstructing wood pulp into a purified fluffy white cellulose. In order to get a good product, special qualities of pulps - dissolving pulps - are used. A common problem with these is that the reactivity of the cellulose is uneven, and the quality of the cellulose acetate will sometimes be impacted. The cellulose is then reacted with acetic acid and acetic anhydride in the presence of sulfuric acid. It is then put through a controlled, partial hydrolysis to remove the sulfate and a sufficient number of acetate groups to give the product the desired properties. The anhydroglucose unit is the fundamental repeating structure of cellulose and has three hydroxyl groups which can react to form acetate esters. The most common form of cellulose acetate fiber has an acetate group on approximately two of every three hydroxyls. This cellulose diacetate is known as secondary acetate, or simply as "acetate". After it is formed, cellulose acetate is dissolved in acetone into a viscous resin for extrusion through spinnerets (which resemble a shower head). As the filaments emerge, the solvent is evaporated in warm air via dry spinning, producing fine cellulose acetate fibers.

Purified cellulose from wood pulp or cotton linters is mixed with glacial acetic acid, acetic anhydride, and a catalyst. The mixture is aged 20 hours during which partial hydrolysis occurs and acid resin precipitates as flakes. These are dissolved in acetone and the solution is purified by filtering. The solution is extruded by spinning in a column of warm air. The solvent is recovered. Filaments are stretched and wound onto beams, cones, or bobbins ready for use. Filaments are finally spun into fiber.

The global production of CA materials was over 800,000 tonnes (790,000 long tons; 880,000 short tons) per year in 2008. Many products are disposed of as litter or into compost. While it was initially believed that CA was virtually non-biodegradable, it has been shown that initial partial deacetylation the polymer's cellulose backbone is readily biodegraded by cellulase enzymes. In biologically highly active soil, CA fibers are completely destroyed after 4–9 months. Photodegradation is optimal with 280 nm or shorter wavelength UV-irradiation and enhanced by TiO₂ pigment. CA cigarette filters take years to be broken down in the open.

2.11. Polyethylene terephthalate

Polyethylene terephthalate (sometimes written poly(ethylene terephthalate)), commonly abbreviated PET, PETE, or the obsolete PETP or PET-P, is the most common thermoplastic polymer resin of the polyester family and is used in fibers for clothing, containers for liquids and foods, thermoforming for manufacturing, and in combination with glass fiber for engineering resins. It may also be referred to by the brand name Dacron; in Britain, Terylene or, in Russia and the former Soviet Union, Lavan.

The majority of the world's PET production is for synthetic fibers (in excess of 60%), with bottle production accounting for about 30% of global demand. In the context of textile applications, PET is referred to by its common name, polyester, whereas the acronym PET is generally used in relation to packaging. Polyester makes up about 18% of world polymer production and is the fourth-most-produced polymer; polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC) are first, second and third, respectively.

PET consists of polymerized units of the monomer ethylene terephthalate, with repeating (C₁₀H₈O₄) units. PET is commonly recycled, and has the number "1" as its recycling symbol.

Depending on its processing and thermal history, polyethylene terephthalate may exist both as an amorphous (transparent) and as a semi-crystalline polymer. The semicrystalline material might appear transparent (particle size less than 500 nm) or opaque and white (particle size up to a few micrometers) depending on its crystal structure and particle size.

The monomer bis(2-hydroxyethyl) terephthalate can be synthesized by the esterification reaction between terephthalic acid and ethylene glycol with water as a byproduct, or by transesterification reaction between ethylene glycol and dimethyl terephthalate with methanol as a byproduct.

Polymerization is through a polycondensation reaction of the monomers (done immediately after esterification/transesterification) with water as the byproduct.

Because PET is an excellent water and moisture barrier material, plastic bottles made from PET are widely used for soft drinks (see carbonation). For certain speciality bottles, such as those designated for beer containment, PET sandwiches an additional polyvinyl alcohol (PVOH) layer to further reduce its oxygen permeability.

Biaxially oriented PET film (often known by one of its trade names, "Mylar") can be aluminized by evaporating a thin film of metal onto it to reduce its permeability, and to make it reflective and opaque (MPET). These properties are useful in many applications, including flexible food packaging and thermal insulation. See: "space blankets". Because of its high mechanical strength, PET film is often used in tape applications, such as the carrier for magnetic tape or backing for pressure-sensitive adhesive tapes.

Non-oriented PET sheet can be thermoformed to make packaging trays and blister packs. If crystallizable PET is used, the trays can be used for frozen dinners, since they withstand both freezing and oven baking temperatures. As opposed to amorphous PET, which is transparent, crystallizable PET or CPET tends to be black in colour.

When filled with glass particles or fibres, it becomes significantly stiffer and more durable. PET is also used as a substrate in thin film solar cells.

Terylene (a trademark formed by inversion of (polyeth)ylene ter(ephthalate)) is also spliced into bell rope tops to help prevent wear on the ropes as they pass through the ceiling.

PET is used since late 2014 as liner material in type IV composite high pressure gas cylinders. PET works as a much better barrier to oxygen than earlier used (LD)PE.

A commentary published in Environmental Health Perspectives in April 2010 suggested that PET might yield endocrine disruptors under conditions of common use and recommended research on this topic.

Proposed mechanisms include leaching of phthalates as well as leaching of antimony. An article published in Journal of Environmental Monitoring in April 2012 concludes that antimony concentration in deionized water stored in PET bottles stays within EU's acceptable limit even if stored briefly at temperatures up to 60 °C (140 °F), while bottled contents (water or soft drinks) may occasionally exceed the EU limit after less than a year of storage at room temperature.

2.12. Polycarbonate

Polycarbonates (PC) are a group of thermoplastic polymers containing carbonate groups in their chemical structures. Polycarbonates used in engineering are strong, tough materials, and some grades are optically transparent. They are easily worked, molded, and thermoformed. Because of these properties, polycarbonates find many applications. Polycarbonates do not have a unique resin identification code (RIC) and are identified as "Other", 7 on the RIC list. Products made from polycarbonate can contain the precursor monomer bisphenol A (BPA).

2.13. Nylon

Nylon is a generic designation for a family of synthetic polymers, based on aliphatic or semi-aromatic polyamides. Nylon is a thermoplastic silky material that can be melt-processed into fibers, films or shapes. Nylon was the first commercially successful synthetic thermoplastic polymer. DuPont began its research project in 1930. The first example of nylon (nylon 6,6) was produced using diamines on February 28, 1935, by Wallace Carothers at DuPont's research facility at the DuPont Experimental Station. In response to Carothers' work, Paul Schlack at IG Farben developed nylon 6, a different formulation based on caprolactam, on January 29, 1938.

Nylon was first used commercially in a nylon-bristled toothbrush in 1938, followed more famously in women's stockings or "nylons" which were shown at the 1939 New York World's Fair and first sold commercially in 1940. During World War II, almost all nylon production was diverted to the military for use in parachutes and parachute cord. Wartime uses of nylon and other plastics greatly increased the market for the new materials. Nylon is made of repeating units linked by peptide bonds. Commercially, nylon polymer is made by reacting monomers which are either lactams, acid/amines or stoichiometric mixtures of diamines (NH_2) and diacids (COOH). Mixtures of these can be polymerized together to make copolymers. Nylon polymers can be mixed with a wide variety of additives to achieve many different property variations. Nylon polymers have found significant commercial applications in fabric and fibers (apparel, flooring and rubber reinforcement), in shapes (molded parts for cars, electrical equipment, etc.), and in films (mostly for food packaging).

3

Functional Fillers

Functional fillers aim to add functions to polymers, such as enhancing mechanical properties, UV or heat stability, thermal or electrical conductivity, dimensional stability, and flame retardancy, without hinder or complicate the compounding process.

This can mean the development and use of special treatment processes – not all fillers display intrinsic properties that can benefit plastic compounds. Many of the newest developments in filler technology for plastics compounds are being driven by the need for lightweighting, particularly in automotive plastics, and for reducing carbon footprint. Selecting the appropriate fillers can improve impact resistance, flexural modulus (stiffness) and maintain ductility at low temperatures. Particle size, shape, aspect ratio and surface treatment are all critical to the performance of functional filler modified compounds.

Examples of functional fillers are talc, iron oxide from hematite, hydromagnesite huntite, wollastonite, precipitated calcium carbonate, ground calcium carbonate with a variety of particle sizes, distributions and coating options [10].

Talc can be used in hydrolytically unstable polymers, such as PLA, polyesters and polyamides, because it picks up water when it is exposed to the air. In a super fine form, talc can be used as a nucleating agent, primarily in polypropylenes.

Hematite filler can be used to add mass in various plastics, such as polypropylene, polyamides and polyethylene. Weight can be useful to impart a high quality feeling to a material or for sound damping. Hematite can also be used as pigment where it can impart an attractive grey metallic sparkle. It also has both magnetic and electrical properties, while its high density makes it x-ray opaque. Hematite filler can be employed to make plastics detectable, for use in medical applications, food processing and for anti-counterfeiting. Due to its high thermal conductivity, hematite can also be added to polymers to allow them to be heated either by microwaves or using induction. Hematite heats up very quickly in a microwave oven, approximately 200°C per minute in a standard domestic oven. While the pure material heats extremely quickly in a microwave, when used as a filler in a plastic this heating capability can be tuned to what is required.

Hydromagnesite huntite filler material has intrinsic flame retardant properties and is halogen free, providing good endothermic fire retardancy and char formation and can be used in a range of polymers such as polyethylene, polypropylene and PVC.

Wollastonite is a cost-effective reinforcing material, with low hydroabsorptivity, good thermal stability and conductivity, low resin demand and chemical purity, providing the following properties (11).

- low linear coefficient of thermal expansion
- surface appearance comparable to painted steel
- excellent impact resistance and elongation (using finer particle size grades)
- improved heat distortion temperature
- improved dimensional stability and reducing shrinkage
- increased flexural modulus
- cost-effective milled glass replacement
- partial replacement for chopped glass

- total replacement of competitive minerals in straight mineral or mineral glass formulations
- low permeability
- excellent weatherability properties
- excellent paintability (on-line, in-line and off-line)
- good flame retardant properties
- creep resistance
- excellent thermal oxidative stability
- low fogging properties

New surface treatments technologies are also being developed that allow existing no functional fillers to deliver improved functionality. The trend is for multifunctional fillers that, in addition to providing filler effects such as reinforcement, adding volume and providing cost reductions, can also provide other enhancements including dispersion, fire retardancy, clarity and anti-scratch effects.

An example of surface area and volume modification additive is the Polyhedral Oligomeric Silsesquioxane (POSS from Hybrid Plastics), a nanostructured product that can improve product performance without sacrificing mechanical properties. POSS chemical technology has two specific features. Firstly, a chemical composition that is a hybrid, intermediate ($\text{RSiO}_{1.5}$) between that of silica (SiO_2) and silicone (R_2SiO). Secondly, POSS molecules are physically large with respect to polymer dimensions and nearly equivalent in size to most polymer segments and coils. POSS silanols are primary surface treatment and react to surfaces in a similar fashion to coupling agents, binding to polar surfaces of powders or key ingredients and ultimately form a Si-O-Metal bond on the surface. No ethanol, methanol or acetate is eliminated, with the reaction from Si-O-H to Si-O-M. A wide range of fillers, such as metals, metal oxides, minerals, colourants, pigments and key ingredients containing polar groups, are suitable for treatment with POSS. It can also aid gloss and colour intensity. POSS affords enhanced dispersion, viscosity reduction at high filler loadings and more effective use of filler. POSS can also bridge the gap between inorganic and organic materials. The hybrid organic-inorganic composition of POSS provides a mechanical inter-phase transition between a rigid/hard inorganic filler and the softer organic resin material. Current compounding equipment needs to provide adequate dispersion of the functional fillers to optimise their reinforcing and processing benefits in a polymer matrix.

Functional filler selection can significantly impact die scrub, wear on machinery, and throughput through improving the thermal conductivity of the mineral-polymer composite.

However, high filler content requires stable, high volumetric dosing and processing die heads are not usually well designed to handle highly filled compounds.

As the key concept for good incorporation of a high degree of fillers in the polymer matrix is volume, the more volume the machinery provides, the easier the handling will be. If this is combined with compounding equipment providing high torque levels, then this is extremely helpful in processing highly viscous materials. High filler content also means a lot of air is inserted in the process, which makes venting and degassing a challenging task for processors. This means that the screw geometries have to be adapted to this task, in addition to the high dispersion needs of the highly filled compound formulations, improving the design of the side feeders in terms of functionality with segmented screws, high volume and better handling (11).

3.1. Glass Fibers

Glass fiber is a material consisting of numerous extremely fine fibers of glass. Glassmakers throughout history have experimented with glass fibers, but mass manufacture of glass fiber was only made possible with the invention of finer machine tooling. In 1893, Edward Drummond Libbey exhibited a dress at the World's Columbian Exposition incorporating glass fibers with the diameter and texture of silk fibers. This was first worn by the popular stage actress of the time Georgia Cayvan. Glass fibers can also occur naturally, as Pele's hair.

Glass wool, which is one product called "fiberglass" today, was invented in 1932-1933 by Russell Games Slayter of Owens-Corning, as a material to be used as thermal building insulation. It is marketed under the trade name Fiberglas, which has become a genericized trademark. Glass fiber when used as a thermal insulating material, is specially manufactured with a bonding agent to trap many small air cells, resulting in the characteristically air-filled low-density "glass wool" family of products.



Figure 4: Glass fibers

Glass fiber has roughly comparable mechanical properties to other fibers such as polymers and carbon fiber. Although not as strong or as rigid as carbon fiber, it is much cheaper and significantly less brittle when used in composites. Glass fibers are therefore used as a reinforcing agent for many polymer products; to form a very strong and relatively lightweight fiber-reinforced polymer (FRP) composite material called glass-reinforced plastic (GRP), also popularly known as "fiberglass". This structural material product contains little or no air or gas, is more dense, and is a much poorer thermal insulator than is glass wool.

Glass-reinforced plastic (GRP) is a composite material or fiber-reinforced plastic made of a plastic reinforced by fine glass fibers. Like graphite-reinforced plastic, the composite material is commonly referred to as fiberglass. The glass can be in the form of a chopped strand mat (CSM) or a woven fabric. [7][8]

As with many other composite materials (such as reinforced concrete), the two materials act together, each overcoming the deficits of the other. Whereas the plastic resins are strong in compressive loading and relatively weak in tensile strength, the glass fibers are very strong in tension but tend not to resist compression. By combining the two materials, GRP becomes a material that resists both compressive and tensile forces well. [9] The two materials may be used uniformly or the glass may be specifically placed in those portions of the structure that will experience tensile loads.[7][8]

3.2. Glass microspheres

Solid and hollow glass microspheres might, in some ways, be seen as a bridge between functional filler and glass fibre reinforcement. Engineered glass microspheres are compounded into a wide range of engineered thermoplastic applications for different purposes. In injection moulded parts that require tight tolerance control, their aspect ratio of 1 can bring dimensional stability and provide warpage control. In parts that will be exposed to harsh working environments they can boost composite modulus and abrasion resistance. And surface modified glass microspheres offer improved bonding with polymer systems [Compounding world, 2017].

In high volume applications using expensive base polymers, engineered glass microspheres can be loaded at higher levels than other mineral type fillers while maintaining lower working viscosities to provide more efficient resin extension and higher cost saving.

Unlike traditional mineral fillers, engineered glass microspheres lower the viscosity of most compounds, acting as miniature internal ball bearings to improve flow. When used in combination with fibres or other particle shapes, mould flow is improved, thus reducing product defects and potentially improving production rates.

Functionally, hollow and solid engineered glass microspheres perform in similar ways in thermoplastics. Solid engineered glass microspheres at 2.5 g/cc density will improve part performance without weight reduction. Hollow engineered glass microspheres (< 1.0 g/cc) offer volume displacement and significant part density reduction.

Aside from density reduction, hollow glass beads are also being considered to improve thermal insulation properties. The glass spheres also have less effect on colour than some tinted mineral fillers.

In thermoplastic processing, hollow engineered glass microspheres demonstrate enough strength to withstand vigorous process conditions without degradation.

Compounding is also said to be straightforward. Due to the smooth, spherical shape of engineered glass microspheres, they require less work to be compounded into resins than angular, irregular, or platelet particles. The engineered glass microspheres have a comparatively low surface area, which keeps working viscosity lower at higher loading levels as well as provides very low resin demand. Engineered glass materials are extremely durable and capable of handling all types of compounding, yet since they are spherical in shape, they will process less harshly and extend equipment life.

Future development work in this type of fillers seems to be focused on development of additional engineered glass microspheres with adhesion promoters to enhance bonding with the polymer matrix [Compounding world, 2017].

3.3. Nanoclay

Nanoclay is the term generally used when referring to a clay mineral with a phyllosilicate or sheet structure with dimensions of the order of 1nm thick and surfaces of perhaps 50-150 nm. The mineral base can be natural or synthetic and is hydrophilic. The clay surfaces can be modified with specific chemistries to render them organophilic and therefore compatible with organic polymers. Surface areas of nanoclays are very large, about 750m²/g. When small quantities are added to a host polymer, the resulting

product is called a nanocomposite. Nanoclays and nanocomposites have generated a tremendous amount of research interest and curiosity, and it is estimated that hundreds of millions of dollars have been invested globally in order to investigate relevant technologies and products. Commercialization has not been rapid to date, but realistically the understanding and development of this concept to and through product stages is detailed and time-consuming. It is likely that nanoclays and nanocomposites will continue to satisfy niche applications and markets and will begin to grow in substantial volume increments as producers and users grow more comfortable with this developing technology. Nanoclays, in addition to their primary function as high aspect ratio reinforcement, also have important additional functions such as thermal and barrier properties and synergistic flame retardancy. Some of the factors responsible for good performance in nanocomposites are as follows:

- Intercalation (surfactant and polymer)
- Interfacial adhesion or wetting
- Exfoliation (dispersion and delamination)

Under appropriate conditions, the gallery spaces can be filled with monomer, oligomer, or polymer. This increases the distance between platelets, swelling the clay. Clay platelets swollen with polymer are said to be intercalated. If the clay swells so much that it is no longer organized into stacks, it is said to be exfoliated.

Indeed, one of the major challenges has been to develop fully exfoliated products to obtain the maximum benefit of nanoclays. During the dispersion process, particles are sheared into tactoids and platelets peel from the tactoids to become fully dispersed or exfoliated in the host matrix. During compounding, important process parameters are clay feed position, type of twin-screw extruder, and screw design/speed. There are numerous publications discussing the effects of process conditions on the degree of exfoliation. A variety of potential host systems including polyamides, polyolefins, PVC, TPU, PLA, EVA, ionomers, rubber, recycled streams, and polymer blends have been evaluated for nanoclays. Although exfoliation has been achieved in many polymers, it has not led to significantly improved mechanical properties other than the modulus. The high degree of interest in the nanocomposite concept has not yet resulted in a plethora of commercial products. However, products are emerging with increasing frequency as producers, processors, and users gain more experience with the products and envisage potential commercial applications. In the case of the nanocomposites used in the 2004 Chevrolet Impala side moldings, General Motors reported a weight savings of 7% as well as a better overall surface quality because the filler is so fine it does not disrupt the surface of the part. The fine fillers are also said to improve mar resistance. Usually, when a stone hits a rocker panel, the white

colour that appears is due to the eye being able to see the filler. In the case of the nanocomposites, this effect should be lessened due to the inherently smaller filler size. As with any new technology and product, challenges had to be overcome. For example, the tooling required some design changes, shrinkage rates were different, and colour recipes needed to be changed. Manufacturing the nanocomposite was also a challenge: introducing a nanoclay at small levels into a TPO requires good distribution and dispersion of the dry product into the polymer melt so that the nanoclay can be substantially exfoliated.

3.4. Carbon Nanotubes

Carbon nanotubes (CNTs) are cylinders of one or more layers of graphene (lattice). Diameters of single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) are typically 0.8 to 2 nm and 5 to 20 nm, respectively, although MWNT diameters can exceed 100 nm. CNT lengths range from less than 100 nm to 0.5 m.

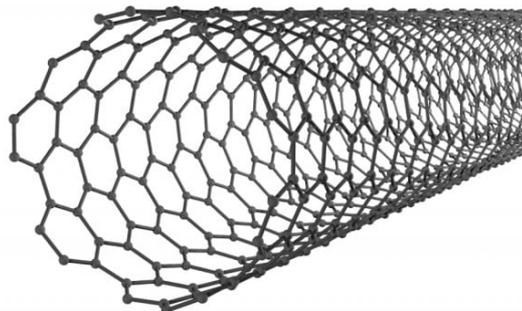


Figure 5: Carbon Nanotube

Individual CNT walls can be metallic or semiconducting depending on the orientation of the lattice with respect to the tube axis, which is called chirality. MWNT's cross-sectional area offers an elastic modulus approaching 1 TPa and a tensile strength of 100 GPa, over 10-fold higher than any industrial fiber. MWNTs are typically metallic and can carry currents of up to 10^9 A cm^{-2} . SWNTs can display thermal conductivity of $3500 \text{ W m}^{-1} \text{ K}^{-1}$, exceeding that of the diamond.

As of 2013, carbon nanotube production exceeded several thousand tons per year, used for applications in energy storage, automotive parts, boat hulls, sporting goods, water filters, thin-film electronics, coatings, actuators and electromagnetic shields. CNT-related publications more than tripled in the prior decade, while rates of patent issuance also increased. Most outputs were of unorganized architecture. Organized CNT architectures such as "forests", yarns and regular sheets were produced in much smaller volumes. CNTs have even been proposed as the tether for a purported space elevator 3D carbon nanotube scaffolds.

Recently, several studies have highlighted the prospect of using carbon nanotubes as building blocks to fabricate three-dimensional macroscopic (>1mm in all three dimensions) all-carbon devices. A novel radical initiated thermal crosslinking method to fabricate macroscopic, free-standing, porous, all-carbon scaffolds using single- and multi-walled carbon nanotubes as building blocks was reported. These scaffolds possess macro-, micro-, and nano-structured pores and the porosity can be tailored for specific applications. These 3D all-carbon scaffolds/architectures may be used for the fabrication of the next generation of energy storage, supercapacitors, field emission transistors, high-performance catalysis, photovoltaics, and biomedical devices and implants.

3.5. Natural Fibers

Natural fibers are also used in composite materials, much like synthetic or glass fibers. These composites are called biocomposites and are a natural fiber in a matrix of synthetic polymers. One of the first biofiber-reinforced plastics in use was a cellulose fiber in phenolics in 1908. Current usage includes applications where energy absorption is important, such as insulation, noise absorbing panels, or collapsable areas in automobiles. Natural fibers can have different advantages over synthetic reinforcing fibers. Most notably they are biodegradable and renewable. Additionally, they often have low densities and lower processing costs than synthetic materials. Design issues with natural fiber-reinforced composites include poor strength (natural fibers are not as strong as glass fibers) and difficulty with actually bonding the fibers and the matrix. Hydrophobic polymer matrices offer insufficient adhesion for hydrophilic fibers

Biocomposite (Latin for 'grown by sun') is a composite material formed by a matrix (resin) and a reinforcement of natural fibers. These kinds of materials often mimic the structure of the living materials involved in the process keeping the strengthening properties of the matrix that was used, but always providing biocompatibility. The matrix phase is formed by polymers derived from renewable and nonrenewable resources. The matrix is important to protect the fibers from environmental degradation and mechanical damage, to hold the fibers together and to transfer the loads on it. In addition, biofibers are the principal components of biocomposites, which are derived from biological origins, for example, fibers from crops (cotton, flax or hemp), recycled wood, waste paper, crop processing by-products or regenerated cellulose fiber (viscose/rayon). The interest in biocomposites is rapidly growing in terms of industrial applications (automobiles, railway coach, aerospace, military applications, construction, and packaging) and fundamental research, due to its great benefits (renewable, cheap, recyclable, and biodegradable). Biocomposites can be used alone, or as a complement to standard materials, such as carbon fiber. Advocates of biocomposites state that use of these materials improve health and safety in their production, are lighter in weight, have a visual appeal similar to that of wood, and are environmentally superior.

3.6. Talc

Talc is widely used as a reinforcement in thermoplastics. It has an anisotropic plate-like shape, which gives it a reinforcing effect in both the machine and cross directions (but with a stronger effect in the machine direction). Talc has better mechanical properties than isotropic minerals, but displays a reduced tendency to cause warping. The hydrophobic character of talc also makes it suitable for easy dispersion in most polymers [Compounding world, 2017].

Highly pure, laminar talc for plastic and rubber enhances the performance of polyolefin compounds such as polypropylene (PP).

The possible applications are virtually infinite. Talc is not only used in automotive plastics and household appliances, but also in food packaging such as acid-resistant keep-fresh packs and yoghurt pots, in laptop housings and in window profiles.

For example, used in PP pipes, say, for sewage water, talc increases rigidity, creep strength and impact resistance (particularly at low temperatures). This makes PP/talc the environmentally friendly alternative to PVC.

In motor vehicles, talc in polymer compounds stabilizes fenders and makes dashboards more scratch-resistant. It gives the plastic parts under the hood the strength they need.

Over the last 20 years, the market for wood-plastic composites (WPCs) has also developed strongly. Here too, talc offers decisive advantages in combination with the natural fibre: it reduces water absorption, shrinkage, deformation and creep. The elasticity modulus and shape retention temperature are improved. Recently, several studies have highlighted the prospect of using carbon nanotubes as building blocks to fabricate three-dimensional macroscopic (>1mm in all three dimensions) all-carbon devices. A novel radical initiated thermal crosslinking method to fabricate macroscopic, free-standing, porous, all-carbon scaffolds using single- and multi-walled carbon nanotubes as building blocks was reported. These scaffolds possess macro-, micro-, and nano-structured pores and the porosity can be tailored for specific applications. These 3D all-carbon scaffolds/architectures may be used for the fabrication of the next generation of energy storage, supercapacitors, field emission transistors, high-performance catalysis, photovoltaics, and biomedical devices and implants.

3.7. Wollastonite

Wollastonite is a calcium inosilicate mineral (CaSiO_3) that may contain small amounts of iron, magnesium, and manganese substituting for calcium. It is usually white. It forms when impure limestone or dolostone is subjected to high temperature and pressure sometimes in the presence of silica-bearing fluids as in skarns or contact metamorphic rocks. Associated minerals include garnets, vesuvianite, diopside, tremolite, epidote, plagioclase feldspar, pyroxene and calcite. It is named after the English chemist and mineralogist William Hyde Wollaston (1766–1828).

Some of the properties that make wollastonite so useful are its high brightness and whiteness, low moisture and oil absorption, and low volatile content. Wollastonite is used primarily in ceramics, friction products (brakes and clutches), metalmaking, paint filler, and plastics.

Despite its chemical similarity to the compositional spectrum of the pyroxene group of minerals—where magnesium and iron substitution for calcium ends with diopside and hedenbergite respectively—it is structurally very different, with a third SiO_4 tetrahedron in the linked chain (as opposed to two in the pyroxenes).

Wollastonite has industrial importance worldwide. It is used in many industries, mostly by tile factories which have incorporated it into the manufacturing of ceramic to improve many performance parameters, and this is due to its fluxing properties, freedom from volatile constituents, whiteness, and acicular particle shape. In ceramics, wollastonite decreases shrinkage and gas evolution during firing, increases green and fired strength, maintains brightness during firing, permits fast firing, and reduces crazing, cracking, and glaze defects. In metallurgical applications, wollastonite serves as a flux for welding, a source for calcium oxide, a slag conditioner, and to protect the surface of molten metal during the continuous casting of steel. As an additive in paint, it improves the durability of the paint film, acts as a pH buffer, improves its resistance to weathering, reduces gloss, reduces pigment consumption, and acts as a flattening and suspending agent. In plastics, wollastonite improves tensile and flexural strength, reduces resin consumption, and improves thermal and dimensional stability at elevated temperatures. Surface treatments are used to improve the adhesion between the wollastonite and the polymers to which it is added. As a substitute for asbestos in floor tiles, friction

products, insulating board and panels, paint, plastics, and roofing products, wollastonite is resistant to chemical attack, inert, stable at high temperatures, and improves flexural and tensile strength. In some industries, it is used in different percentages of impurities, such as its use as a fabricator of mineral wool insulation, or as an ornamental building material.

Plastics and rubber applications were estimated to account for 25% to 35% of U.S. sales in 2009, followed by ceramics with 20% to 25%; paint, 10% to 15%; metallurgical applications, 10% to 15%; friction products, 10% to 15%; and miscellaneous, 10% to 15%. Ceramic applications probably account for 30% to 40% of wollastonite sales worldwide, followed by polymers (plastics and rubber) with 30% to 35% of sales, and paint with 10% to 15% of sales. The remaining sales were for construction, friction products, and metallurgical applications. The price of raw wollastonite varied in 2008 between US\$80 and US\$500 per tonne depending on the country and size and shape of the powder particles.

3.8. Wood flour

Wood flour is finely pulverized wood that has a consistency fairly equal to sand or sawdust, but can vary considerably, with particles ranging in size from a fine powder to roughly the size of a grain of rice. Most wood flour manufacturers are able to create batches of wood flour that have the same consistency throughout. All high quality wood flour is made from hardwoods because of its durability and strength. Very low grade wood flour is occasionally made from sapless softwoods such as pine or fir. Wood flour is commonly used as a filler in thermosetting resins such as bakelite, and in linoleum floor coverings. Wood flour is also the main ingredient in wood/plastic composite building products such as decks and roofs. Prior to 1920, wood flour was used as the filler in ¼-inch thick Edison Diamond Discs.

3.9. Calcium carbonate

Calcium carbonate (CaCO_3) is one of the most popular mineral fillers used in the plastics industry. It is widely available around the world, easy to grind or reduce to a specific particle size, compatible with a wide range of polymer resins and economical. As an additive in plastic compounds, CaCO_3 helps decrease surface energy and provides opacity and surface gloss, which improves surface finish. In addition, when the particle size is carefully controlled, CaCO_3 helps increase both impact strength and flexural modulus (stiffness).

Calcium carbonate may be used with a myriad of thermoplastic resins. Polypropylene compounds are often filled with calcium carbonate to increase rigidity, an important requirement for operations at high temperatures. In PVC, calcium carbonate is used with flexible compounds such as tubing, wire and cable insulation, latex gloves, trash bags and in rigid compounds such as extruded pipes, conduits and window profiles. The design of a feeding or pneumatic conveying system is heavily influenced by a bulk solid's particle shape, size (aspect ratio) and particle size distribution as well as the particle's roughness, hardness (abrasiveness), and density. In the case of calcium carbonate these characteristics vary widely depending on the source and production process for the individual samples.

The sieve analysis below illustrates the difference in particle shape, particle size and particle size distribution for two samples of calcium carbonate.

The large number of particle interactions makes it impossible to establish a clear correlation between filler's properties at the particle level and its flow behaviour as a bulk solid.

As a consequence, pneumatic conveying systems cannot be purchased "off-the-shelf" and must be engineered for each situation individually. Both systems engineering and equipment selection are affected by differences in a bulk solid's characteristics. Laboratory tests are often necessary to help determine a material's properties and behaviour. A pneumatic conveying system generally consists of five basic components: a gas motive, a conveying line, a dispensing device, a material-gas separator and controls. When selecting a dispensing device, it must be taken into consideration that some grades of CaCO_3 are light and fluidizable and may flood convey lines. In such cases, a rotary valve should be considered to meter the material into the line. Rotary valves can be used for pick up in either pressure or vacuum pneumatic conveying systems. With adhesive grades of CaCO_3 the product will tend to build up and not release from the blades of a drop-through rotary valve. In this case a blow-through style rotary valve is necessary; air is blown through each pocket as the valve turns, dislodging material from the blades. The installation of a fluidizing cone in the feed bin is also helpful in controlling the flow of the material.

Calcium carbonate powders can cause many problems in conveying systems, including sticking in hoppers, flood feeding into convey lines, building up inside convey lines, and blinding over filter bags and cartridges in receivers. Rigid pipes may be used as a convey line for highly fluidizable to slightly adhesive CaCO_3 . However, if the CaCO_3 tends to coat the interior of the convey line, a flexible hose could be considered because flexing of the line helps prevent build-up on the walls of the hose.

In vacuum sequencing systems, it is a good precaution to use a purge valve to allow the line to clear between conveying sequences. First, a shut-off valve at the pickup of a vacuum system is closed to allow vacuum to build in the line. Then the valve is opened, creating a pressure wave that helps clean off any coating of material adhering to interior surfaces of the convey line. Often CaCO_3 will adhere to the filter, causing it to blind over and reduce filter efficiency. For sticky grades of CaCO_3 using filter bags instead of pleated filter cartridges may help reduce the tendency of the CaCO_3 to stick to the filters. In extreme cases the use of PTFE filter media is recommended.

Some calcium carbonate grades may require a steeper discharge cone in order to allow complete emptying of the hopper. Flow aids such as vibrators or fluidizing pads inside the receiver hopper will usually help ensure quicker and more complete discharge of the receiver.

The sieve analysis illustrates the difference in particle shape, particle size and particle size distribution for two samples of calcium carbonate. While Sample A is a precipitated calcium carbonate (PCC) with a relatively low bulk density, Sample B is a granular calcium carbonate with a much higher bulk density.

3.10. Fire retardant

Fire retardant additives are very important for the construction sector.



Figure 6: Burning Grenfell Tower in London

In the following the most important fire retardants are described. Metal hydroxides, particularly aluminum trihydrate and magnesium hydroxide, contribute to several fire-retardant actions. They first decompose endothermically and release water. The endothermic decomposition serves to remove heat from the surroundings of the flame and, thus, cool the flame. This is often referred to as the “heat sink” phenomenon. Pyrolysis decreases in the condensed phase as a result of this action. The release of water dilutes the amount of oxygen capable of ingress to the flame and avoids the critical fuel/oxygen ratio (physical action in the gas phase). Both mechanisms combat ignition. In some fire tests used for electric/electronic, cable applications, the ignition has to be significantly delayed. Thus, metal hydroxides are suitable for these applications. Moreover, after the degradation, a ceramic-based protective layer is created that improves insulation (physical action in the condensed phase) and gives rise to a smoke suppressant effect (chemical action in the condensed phase). The ceramic-based protective layer ensures an efficient protection of the polymer during combustion leading to a severe decrease in the heat released.

Zinc borate can be used as a fire retardant in PVC, polyolefins, elastomers, polyamides, and epoxy resins. In halogen-containing systems, it is used in conjunction with antimony oxide, while in halogen-free systems it is normally used in conjunction with other FRs such as aluminum trihydrate, magnesium hydroxide, or red phosphorus. In a small number of specific applications, zinc borate can be used alone.

Melamine (2,4,6-triamino-1,3,5-triazine) or melamine-derived flame retardants represent a small but fast growing segment in the flame-retardant market. In this family, three chemical groups can be defined; pure melamine, melamine derivatives, that is, salts with organic or inorganic acids such as boric acid, cyanuric acid, phosphoric acid or pyro/poly-phosphoric acid, and melamine homologues containing multiring structures. Melamine-based flame retardants show excellent flame-retardant properties and versatility in use because of their ability to employ various modes of flame retardant action. Melamines are only briefly mentioned in this chapter since they may be considered as additives rather than true functional fillers.

The element phosphorus (red phosphorus) is known to be an effective inhibitor of combustion. A wide variety of phosphorus-containing materials are used as fire retardants in a broad range of polymers from elemental red phosphorus to both inorganic and organic compounds such as ammonium polyphosphates, organophosphates, and phosphinates, phosphorus-nitrogen compounds such as melamine phosphates, phosphorus-halogen compounds, and phosphorus-containing polyols that are used to produce polyurethane foams. Phosphate esters, with or without halogen, are widely used in PVC or in polymers that have high hydroxyl group content. The level of phosphorus in different chemicals can vary from below 10% to close to 50% in the case of red phosphorus. The oxidation state of the phosphorus can range from 0 to $+5$.

3.11. Conductive Fillers

Polymers are often the favored materials for the manufacture of devices and components. They combine ready formability and molding characteristics with good insulating and dielectric properties. These attributes are sufficient to make plastics and elastomers functional for many purposes. But in some instances, it would be desirable to have polymers that could dissipate static charges or shield their contents from electromagnetic fields. In other applications, the control of static charge (as in xerography) or control of conductivity as a function of current density (self-limiting switches and heaters) is attractive. All of these functions have been achieved by the addition of conductive fillers to polymers. In this chapter we describe some of these applications and the roles played by functional fillers in controlling polymer conductivity.

In a similar manner, we will discuss how to confer the properties of permanent magnetization on polymers through composite materials consisting of a magnetic solid dispersed in a polymer matrix or binder. These range from the familiar refrigerator magnets and magnetic recording tape to data disks that can store information at very high densities.

It is widely observed when adding carbon black (CB) to an insulating polymer that there is a threshold concentration, V_c , at which the composite changes from insulating to conductive. Conductivity (and resistivity) change by several orders of magnitude for a small increment in carbon black concentration. This threshold, which typically occurs from 3 to 15% CB, has been the subject of many investigations.

Unfortunately, in these systems there are not only many independent variables such as the surface chemistry and dispersibility of various blacks but, to complicate these studies, there are also significant effects of polymer interfacial chemistry, various modes of compounding and segregation to phase boundaries. We attempt to elucidate several of these effects by examples from the literature. Our selections are not all-inclusive and do not attempt to address the very large patent literature in this field.

3.12. Processing Aids

Processing aids are materials that are added to improve the processability of polymeric compounds, increasing softening, decreasing melting or glass transition temperature and decreasing viscosity to help flow during processing. Improved processability lowers the cost and improves the quality of the polymer. With the help of processing aids, extrusions run thinner and faster and molding cycles shorten. PVC's, polyolefins, nylons and other engineering plastics are known to benefit the most from the addition of processing aids. Most used processing aids are styrenes, acrylics, lubricants, silicone oils etc..

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