



NANOFILLERS - IMPROVING PERFORMANCE AND REDUCING COST

Fillers are one of the most common raw materials in the world with 50 million tonnes produced every year¹. Fillers are mainly utilised to reduce the consumption of expensive binder material and to improve the physical properties of the resulting composite material. They are widely used in paper, rubber, plastics, adhesives & sealants, paints & coatings, and also in concrete. Today fillers are undergoing a paradigm shift; their former primary function to lower the production costs is changing towards a distinct tuning of material properties such as compression strength, processability, and flame retardancy. This is especially true for ultra-fine grades or so called nanofillers which provide an improvement in properties such as material reinforcement due to their larger surface area. In general, a smaller filler particle size will have a greater impact on the material properties when the particles are properly dispersed. Therefore, nanofillers may provide a route towards future material innovations, cost efficiency, and competitiveness. This BRIEFING will discuss the purpose, uses and potential of a number of nanofillers before examining the economic impacts and challenges facing their route to wider commercialisation.

Background

Nanofillers can be either small spherical particles or rod shaped objects and flakes with at least one critical dimension below 100nm. In general, the properties of filler materials are determined through particle size, particle geometry and chemical coatings, or functionalisation. Smaller particles provide new functionalities such as control of rheological properties, improved mechanical properties, an increased transparency or electrical conductivity, or enhanced flame retardancy. They can be also used to ensure the free flow of powders and to prevent the settling of pigments. Fillers are widely used in the construction sector in adhesives and sealants, in paints and coatings, but also in plastics, rubber and concrete.

Synthetic fillers are now gaining more importance; they allow the production of smaller particle sizes with controlled surface chemistry or tailored chemical functionalisation. Ultra-fine grades or so called nanofillers are under investigation. Besides downsizing existing filler materials, completely new technological approaches can also be observed such as organic-inorganic hybrid materials in polymers or nanotubes as reinforcing filler material in concrete. However, the share of nanofillers in today's construction filler market is negligible. An example of well established nanofillers can be found in another sector; carbon black filled tyres for longer life and improved performance.

Particle Size

The filler particle size determines the "inner" or specific surface area which is the potential contact area between filler material and surrounding binder matrix. Since nanomaterials tend to agglomerate or may already occur in agglomerated states, the resulting surface area is largely affected by the degree of exfoliation and dispersion. Fully exfoliated and perfectly dispersed nanofiller will

have the greatest effect on the physical properties.

A comparison between different particle sizes is shown in **Figure 1**. The specific surface area is increased 100-fold when going from 10 μ m to 100nm while keeping the theoretical volume or the filling level constant.

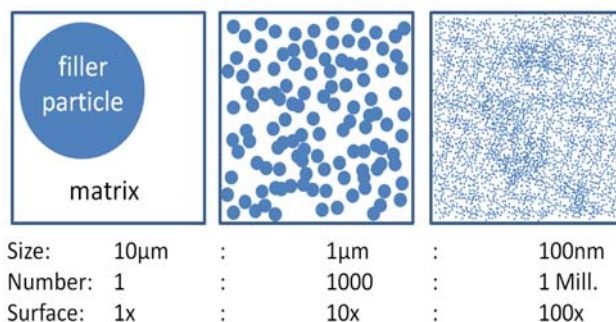


Figure 1: Different filler particle sizes at the same filling level. Going from 10 μ m to 100nm: a million times more particles exhibit a 100-fold increased inner surface area (adapted from ²).

Geometry

The particle geometry will also strongly influence the properties of the nanocomposite material. Elongated nanostructures such as carbon nanotubes exhibit high aspect ratios. Higher aspect ratios will increase the reinforcing ability on the surrounding matrix material. Therefore nanotubes or other elongated nanofillers excel over spherical particles in terms of reinforcement. Nanotubes can be considered as (quasi-)one-dimensional filler particles in terms of reinforcement. Similar nanomaterials are nanowhiskers³, nanorods, nanowires and nanofibres which have also been reported as nanoscopic reinforcing filler material for polymers. Natural occurring representatives of a two dimensional filler material are layered silicates or so called nanoclays. The most widely used nanoclays in material applications are so called montmorillonites as flame retardant in polymers.

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A common approach is the production of three-dimensional filler particles by either grinding, milling or precipitation techniques. In contrast, also bottom-up approaches have been studied where the filler material is incorporated as a building block on the molecular level. This case can be regarded as zero-dimensional nanofillers. In this regard inorganic-organic hybrid materials have been investigated intensively. **Figure 2** gives an overview of the different filler particle geometries.

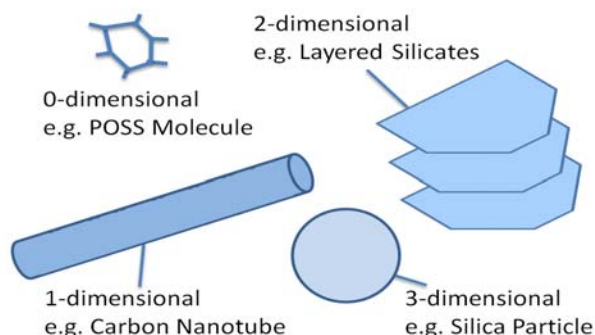


Figure 2: Different filler particle geometries.

POSS molecules

Polyhedral oligomeric silsesquioxane (POSS) molecules represent a comparatively new approach as a building block for new nanocomposite materials. The biggest advantage of using a molecular approach can be found in a true dispersion at the nanometre level. POSS molecules can be used as reinforcing filler in plastics to increase the mechanical strength. They are also relevant as abrasion protection in paints and coatings and as fire retardant material in polymers.

Precipitated Calcium Carbonate (PCC)

Calcium carbonate (CaCO_3) is by far the most widely used filler material in the world, particularly as a filler in paper and plastics. Traditionally, CaCO_3 is mined from natural resources (limestone and processed by milling techniques. The resulting material is therefore called ground CaCO_3 (GPP). Its synthetic counterpart is called precipitated CaCO_3 (PCC) exhibiting finer particles sizes and smaller particle size distribution. It is available in fine and ultra-fine grades whereby the latter one is sometimes referred to as nano-precipitated CaCO_3 . Particles sizes range from 60nm to 150nm. It is used as filler in adhesives and sealants to adjust the rheological properties and also in plastics to improve mechanical strength and durability.

Fumed Silica

Fumed or pyrogenic silica is a form of non-crystalline silicon dioxide. Primary particle sizes are between 5-30 nm which aggregate into larger agglomerates while maintaining a fairly large specific surface area of 10-600 m^2/g .⁴ Fumed silica is widely used as anti-caking additive and thickening agent with thixotropic property (becomes liquid

when stirred or shaken but return to original state when at rest). It is also used in paints, coatings, adhesives and sealants but also as filler in plastics and rubber. Many different untreated and treated grades with varying properties are on the market today. Fumed silica is also used in thermal insulation material such as vacuum insulation panels⁵.

Precipitated Silica

Precipitated silica is produced from aqueous sodium silicates precipitated with sulphuric acid. In contrast to fumed silica precipitated silica consists of porous particles with a primary particle size of about 5-100 nm which form large agglomerates of several micrometres. The specific surface area can be as high as 200 m^2/g .⁶ Precipitated silica is mainly used as reinforcing filler in the rubber industry but also as filler in plastics and sealants (silicone rubber) and adhesives (epoxy).

Precipitated Barium sulphate

Precipitated barium sulphate (BaSO_4) is called "Blanc fixe" due to its whitening ability. It is used as brightener or white pigment. Blanc fixe is mainly used as filler in paints and coatings but also in plastics. The production of ultrafine or nano-precipitated barium sulphate (nanoPBS) has been investigated recently⁷. However, particle sizes of Blanc fixe are generally well above the nanometre range so is not considered as nanomaterial.

Titanium Dioxide

Titanium dioxide (TiO_2) is naturally occurring in three different forms; rutil, anatase, and brookite. Rutil is mainly used as white pigment in paints and coatings while the anatase modification is widely used in photocatalytic applications. TiO_2 is also used as filler in silicone rubber⁸ and thermoplastics such as PVC.

Nanoclays

Nanoclays are plate-like nanoparticles of natural occurring layered silicates. Clay minerals are divided in numerous classes such as bentonites or hectorites. Bentonites mainly consist of so called montmorillonites, the most widely used nanoclay in material applications today. Montmorillonites are build up of stacked nanoscopic aluminosilicate plates each around 1nm in height and 1 μm in diameter and are used as filler in plastics. Organically modified montmorillonites, so called organoclays, are used to increase the flame retardancy of polymers especially in cables; the flame propagation is significantly reduced and no dripping of burning polymer is observed⁹. However, aluminium trihydroxide (ATH) currently dominates the world market for fire protection agents.

Carbon nanotubes

Carbon nanotubes (CNT) have been investigated intensively due to their unique mechanical and

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electrical properties. A key application of multi-walled carbon nanotubes (MWNT) is seen as functional fillers in plastic composites and paints¹⁰. They have been also studied as reinforcing filler in concrete and have been proven to prevent crack propagation¹¹.

Carbon Black

Carbon black (CB) is a (nano-) particulate amorphous form of carbon, mainly used as a filler in rubber and as pigments. It is also used as a filler in plastic and paints to induce electrical conductivity. It has additionally been proven as a UV-stabilizer in plastics application improving the weatherability¹². However, the market for non-rubber applications is comparatively small.

Graphene

Besides Carbon black, graphite is also used as filler in paints and coatings inducing electrical conductivity, thereby obtaining antistatic property. Its 2-dimensional counterpart is called graphene which can be considered as a single sheet of graphite. Graphene could also serve as filler for conductive and reinforcing applications; however, research and production techniques are still in their infancy.

Aerogels

Aerogels are nanoporous materials with the lowest bulk density of all solids. They have been investigated as thermal insulation material due to their extremely low thermal conductivity. In granular form aerogels can also be used as filler in concrete forming a lightweight construction material with unique thermal properties¹³.

Economic impacts

The global filler market was about 50 million tonnes in 2006 with a market size of around €25 billion. Europe ranked second with 15.5 million tonnes after Asia with 19 million tonnes. The annual growth rate of the European filler market is about 3%¹. Fillers represent one of the largest technical materials in the world; however, today's nanocomposite market is comparatively small (**Figure 3**). Nevertheless, the global nanocomposite market

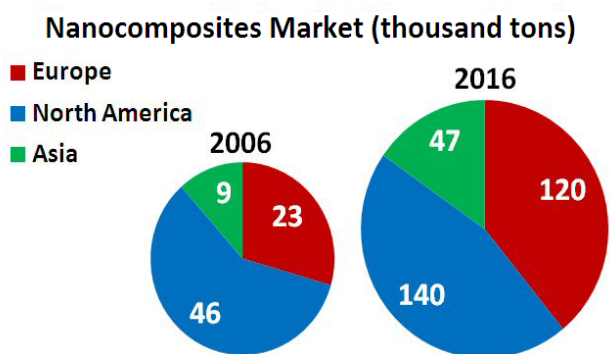


Figure 3: The European market for nanocomposites is predicted to grow from 23 000 tonnes (2006) to 120,000 tonnes in 2016¹.

size is predicted to increase to €1.47 billion by 2015¹⁴. Market figures differ depending on the classification of nanocomposite materials and source though.

The world market for precipitated CaCO₃ was 13 million tonnes in 2007¹⁵, mostly due to the paper industry. The share of nanoscale precipitated CaCO₃ is significantly smaller; one of the world's biggest producers is the Chinese based ShengdaTech with a current production capacity of 250000 tonnes. The world market of fumed silica reached €980 million in 2010. Major producers include German based Evonik and Wacker together with US-based Cabot and Japanese Tokuyama (**Figure 4**).

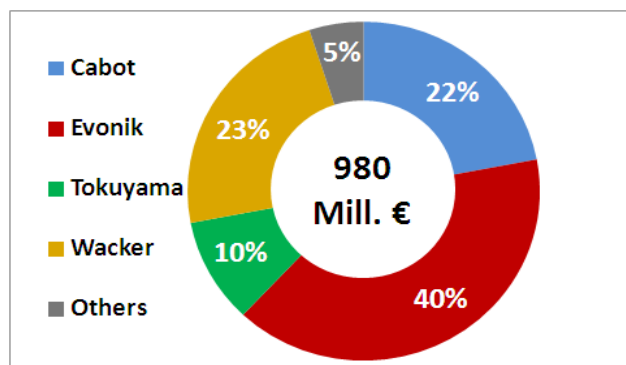


Figure 4: Fumed silica market 2010 by company (adapted from¹⁷).

The world market of CNT is expected to grow from €1.6 billion in 2010 to €3.3 billion in 2016¹⁸. Major producers are US based Cnano, Belgium based Nanocyl and German based Bayer Materialscience with a production capacity of 500 tons, 460 tonnes and 200 tonnes respectively. French based Arkema has announced to boost its production capacity to 400 tonnes within a short time. The global nanoclay market was around €139 million in 2009 and is predicted to grow moderately to around €208 million by 2015¹⁹. Major manufacturers include the US based Nanocor, Chinese based FCC Inc and UK based Elementis Specialities plc amongst others.

The biggest manufacturer of precipitated silica is Rhodia based in France. Other producers are Evonik, Germany, PPG Industries and Tulco Inc US, and Wuxi Quechen Silicon Chemical Co.,Ltd. China.

EU Competitive Position

The nanocomposite market is mainly driven by the US and Europe. The US is the present leader; however, Europe and Asia are predicted to catch up in coming years. Europe also having a strong position in the production of CNT. Regarding fumed and precipitated silica Europe is leading followed by the US and Asia; however, Europe's position is weak in nanoclays and nanoscale CaCO₃. Asia leads the graphite and carbon black sectors.

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Technology Readiness Levels



Figure 5: TRL levels indicating the development level of filler technologies.

Challenges

Technological

A major barrier for the wider commercialization of nano-enabled fillers is the poorer dispersion ability of ultra-fine grades or nanomaterials. In this regard, a suitable treatment or functionalisation of nanoparticles or aggregates depending on the intended use is helpful. In addition, higher costs of raw materials and treated grades are a disadvantage. An increase in the brittleness of nanocomposites with high filling degrees has also been observed. Further key challenges include exfoliation and dispersion of nanomaterials.

Environmental, Health & Safety Implications

Nanomaterials in powder form can easily become airborne. For fillers, this applies at the stage of both material production and of composite production and processing. Nanomaterials used as fillers include both high volume production materials for which there is already considerable history of toxicity research (e.g. PCC, silica), as well as new materials (e.g. CNT, graphene) for which potential hazard has been highlighted and is currently subject to extensive investigation. Excessive exposure to any of these nanomaterials has potential to result in risks to health and the environment. Whilst for many of these materials (e.g. PCC), previous exposures have been observed with no significant ill effects, for some new materials (e.g. CNT), a potential for much greater toxicity has been identified, particularly with respect to inhalation exposure. In line with the precautionary principle, appropriate occupational health and safety mechanisms should therefore be in place in order to prevent exposure. Life cycle assessments, including recycling processes, are also required to prevent

long-term environmental implications.

Summary

- Nanofillers are characterized by their particle size, specific surface area, particle geometry and chemical functionalisation.
- Smaller filler particle sizes provide new functionalities such as improved mechanical strength and control of rheological properties.
- The high specific surface area of nanomaterials provides a route towards novel properties and decreased filling levels.
- Needle-like nanofillers have a stronger impact on the mechanical properties.
- Hybrid materials provide a route towards fully dispersed nanomaterials and superior nanocomposites.
- Critical issues are exfoliation and dispersion of nanomaterials, and a poorer processability.
- Due to some EHS concerns, appropriate occupational health and safety mechanisms should be in place in order to prevent exposure.

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References

- ¹ Market Report "Fillers" (Marktstudie Füllstoffe (UC-805)), Ceresana Research, 2007.
- ² „Reinforcing mechanisms on the macro-, micro- and nanoscale in heterogeneous polymer materials“ (Verstärkungsmechanismen auf Makro-, Mikro- und Nano-Längenskalen in heterogenen Polymerwerkstoffen), Habilitation thesis, Gyeong-Man Kim, University of Halle
- ³ Yang Li and Arthur J. Ragauskas, [Advances in Diverse Industrial Applications of Nanocomposites](#), ISBN 978-953-307-202-9, [InTech](#), March 2011
- ⁴ <http://www.freepatentsonline.com/20040253164.pdf>
- ⁵ „MICRO-NANO POROUS MATERIALS FOR HIGH PERFORMANCE THERMAL INSULATION“ CSTB French Building Research Institute, 2nd International Symposium on Nanotechnology in Construction, Bilbao 2005.
- ⁶ <http://www.iri.net.in/conference/images/stories/pdf/IRI/Presentation/Technical/18/3/Laurent.Guy.EA.090.pdf>
- ⁷ „Precipitation of Barium Sulphate Nanoparticles in Microemulsion: Experiments and Modelling“, PhD thesis of Dendy Adityawarman, University of Magdeburg.
- ⁸ G. Momen and M. Farzaneh, *Rev. Adv. Mater. Sci.* 27 (2011), 1-13.
- ⁹ <http://belgianpolymergroup.be/Flame/Beyer.pdf>
- ¹⁰ J.M. Makar and J.J. Beaudoin, Proceedings of 1st International Symposium on Nanotechnology in Construction June 23-25, 2003, Paisley, Scotland
- ¹¹ Raki, L. et al, *Materials* 2010, 3, 918-942
- ¹² J. V. Accorsi, *KGK Kautschuk Gummi Kunststoffe* 54. Jahrgang, Nr. 6/2001
- ¹³ Lorenz Ratke, *Beton- und Stahlbetonbau* 103 (2008), Heft 4
- ¹⁴ <http://www.electronics.ca/presscenter/articles/1404/1/Global-Nanocomposites-Market-to-Reach-13-Billion-Pounds--by-2015/Page1.html>
- ¹⁵ <http://www.roskill.com/reports/industrial-minerals/pcc/>
- ¹⁶ <http://www.shengdatechinc.com/files/09-07-09%20SDTH%20profile.pdf>
- ¹⁷ <http://www.wacker.com/cms/media/documents/investor-relations/factbook2010.pdf>
- ¹⁸ „Global Carbon Nanotube Market - SWCNT, MWCNT, Technology, Applications, Trends & Outlook (2011 - 2016)“ published by Market-sandMarkets (<http://www.marketsandmarkets.com>)
- ¹⁹ <http://www.marketresearch.com/product/display.asp?productid=2873964>