

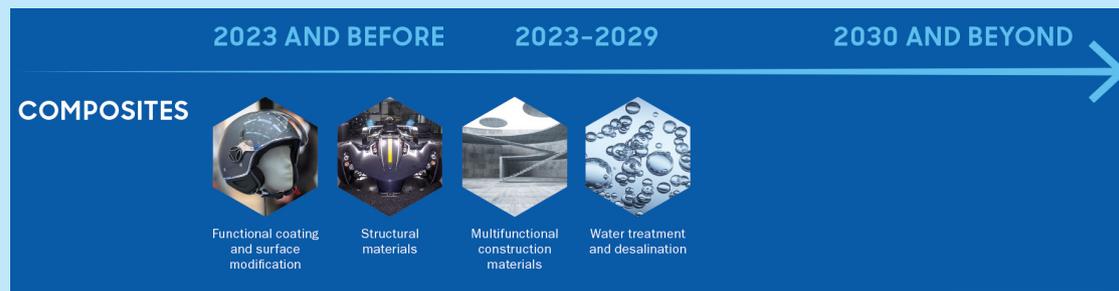
# The Graphene Flagship Technology and Innovation Roadmap

## Composites, Bulk Applications and Coatings

The Composites, Bulk Applications and Coatings section of the Graphene Flagship Technology and Innovation Roadmap covers the use of graphene and other 2D materials as bulk materials, additives to composite materials and coatings.

Graphene and related 2D materials have attracted substantial investment and resources over the last decade for their development into the next generation of composite materials. This is due to the potential of these nanomaterials to act as reinforcing additives capable of simultaneously imparting significant mechanical property enhancements as well as embedding multi-functional benefits on the host matrix.

The potential markets for these application areas are very wide by definition. Essentially, the enhanced composites or coatings can be used in any market that relies on or benefits from material developments.



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## **3 Composites, bulk applications and coatings**

### **3.1 Potential composites, bulk and coatings applications**

This chapter covers the use of graphene and other 2D materials as bulk material, as additive to composite materials and as coating. The focus is on structural materials and materials that offer functionalities such as electrical and thermal conductivity, barrier and additional mechanical properties. This chapter covers all bulk applications besides the ones dealing with electronics and energy generation and storage (see chapters 4 Energy generation and storage and 5 Electronics & Photonics). These application areas are summarized in Figure 26.

The basic idea is to use the 2D materials to improve or enhance the properties of the host bulk material, e.g. a polymer, ceramic, or to improve the surface by making use of the interesting properties of graphene as a coating. Besides, graphene and 2D materials can also be used as an additive to fluids to enhance the properties or to fulfil a particular function, e.g. to act as an absorber for unwanted materials (remediation).

In the area of composites, bulk applications and coatings, graphene materials are mostly used as an additive or as a coating in form of bulk powders or flakes: few-/multilayer graphene, graphite nanoplatelets, graphene nanoribbons or (reduced) graphene oxide. For coatings, also films (mostly few layer) are of importance. 2D materials are also investigated to be used as membranes, e.g. for filtering. Often the difference between graphene materials and nano-graphite is blurry.

The potential markets for these application areas are very wide by definition. Essentially, the enhanced composites or coatings can be used in any market that relies on or benefits from material developments. An overview of potential markets will be given in each subsection on the particular application area.

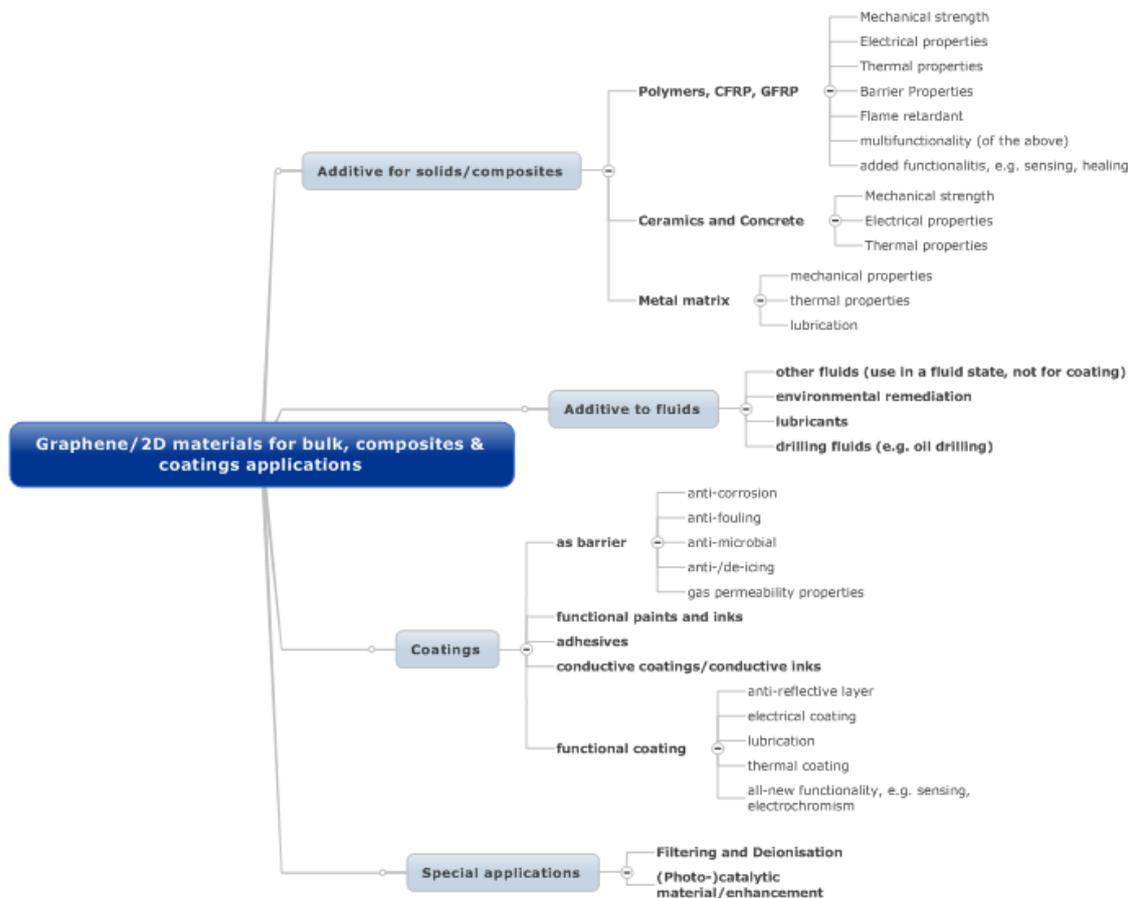


Figure 26: Potential applications of graphene and 2D materials covered in this chapter.

### 3.2 Additive to bulk solids/composites

Graphene or other 2D materials can be used as an additive or filler for composite materials. The rationale for this application is to improve the properties of the bulk host material by making use of the interesting properties of graphene or other 2D materials (e.g. mechanical strength, electrical or thermal conductivity, etc.), compare Figure 27 and Table 7. Typical host materials are polymers, carbon-reinforced polymers, ceramics, concrete, etc. where the addition of graphene/2D materials shall improve particular mechanical and functional properties usually addressing a weakness of the host material.

Table 8 summarizes potential host materials and the addressed weaknesses. Figure 28 gives an overview of mechanical properties (Young's modulus) of potential host materials. Usually the improvements need to be achieved whilst the original other properties, including the processability of the host material, remain largely unaffected and should not be impaired.

Typically competing technologies/materials are the usually used additives/filler materials, metals, other nanomaterials and other carbon based additives and, such as carbon black, soot, graphite nanoflakes or carbon nanotubes (CNT).

This chapter focuses on bulk materials and their improvements, referring to the use in the body/bulk of a component through dispersion of the additive. This is in contrast to coatings and paints, which are only applied to a surface of a body/bulk material. There are indeed some overlaps with coatings and paints, in particular with respect some potential property improvements and functionality. These can sometimes be achieved in both ways, by using a coating or adding 2d materials to the bulk (properties marked with \* in Table 7).

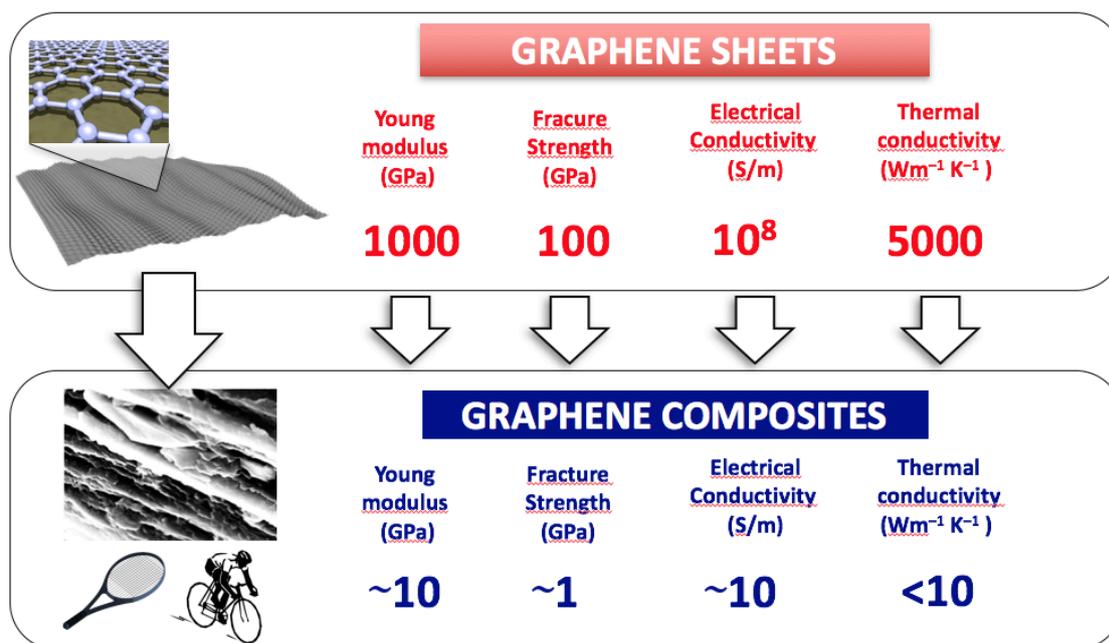


Figure 27: Properties of graphene sheets and current realisation in composites. [118–120]

Table 7: Composite property improvement and application areas. The properties with \* can also potentially be achieved with coatings.

<b>Composite property improvement</b>	<b>Target application areas</b>
Mechanical properties	Structural applications, improved strength of conventional lightweight materials, improved tensile strength, impact toughness, elasticity, fracture toughness, wear resistance
Electrical conductivity ( $\sigma$ )*	EMI shielding, antistatics, electro-machining, signal/power transmission, functional lightweight materials, field grading materials, electrical toughness/dielectric strength
Thermal conductivity ( $\kappa$ )*	Heat dissipation/heat removal through increased thermal conductivity. Metal replacement for heat exchangers where corrosion resistance and light weight are required.
Barrier properties*	Gas barriers, flame retardancy
Surface area/properties*	Catalysis, tribological properties (lubrication/friction, look & touch & feel, anti-squeak)
Multi-functional property enhancement*, added functionalities	All areas where a combination of the above properties are beneficial, as well as added functionalities such as damping, self-healing, damage detection etc.

Table 8: Host materials for composites, weaknesses addressed by graphene/2D material addition and recent reviews on the topic.

Host material	Sub category	Main weakness of host addressed	Recent review
Polymers	Elastomers	Insulating, mechanical strength, fracture toughness, thermal conductivity <sup>f</sup>	[121]
	Thermoplastics		[118, 122]
	Thermosets, fibre-reinforced polymers		
	Adhesives		[123, 124]
Metals	e.g. Al, Cu, metal matrix composites	Weight and/or mechanical strength, functionality (e.g. for batteries)	[125, 126]
Ceramics		Brittle, electr. insulating, fracture toughness	[127]
Concrete/Cement		flexible/tensile strength, strain, brittle/crack formation, electr. insulating	[128]

<sup>f</sup> Thermal interface materials are covered in chapter 3.3 and 5.2 Electronics: Cross-cutting issues.

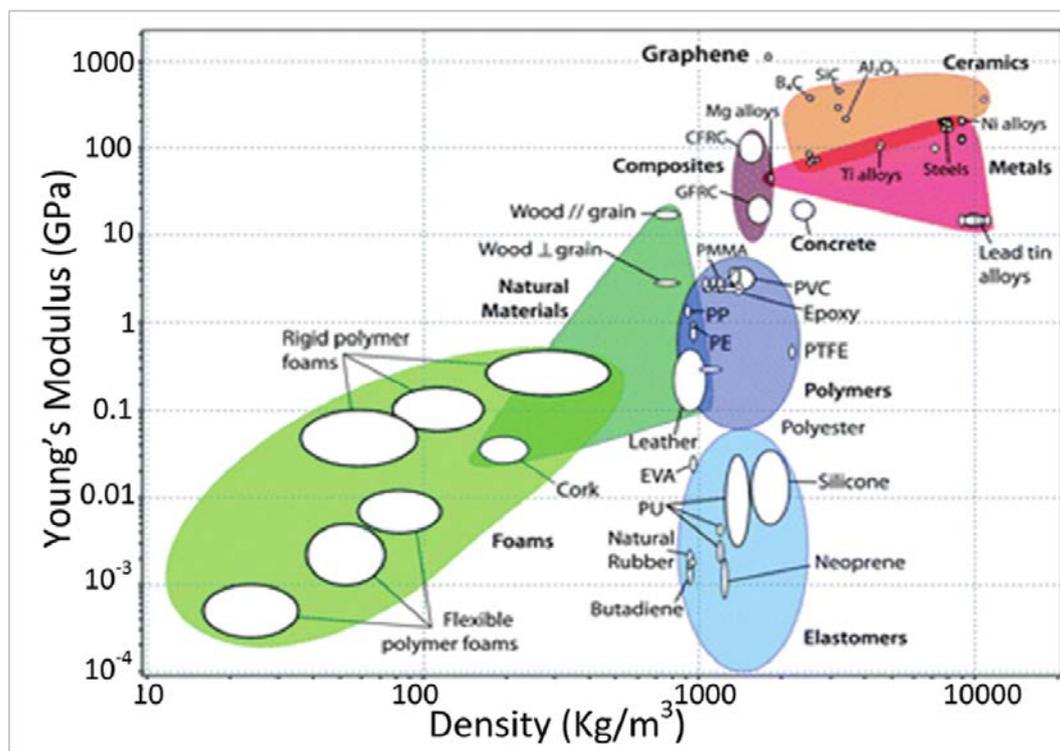


Figure 28: Young's modulus of several potential host materials and of pristine graphene. [129]

Other 2D materials, such as two-dimensional Boron Nitride (BN), Magnesium-Hydroxide or Molybdenum Disulfide (MoS<sub>2</sub>) and other transition metal dichalcogenide (TMD) monolayers also offer interesting functionalities. BN for instance offers barrier properties and thermal conductivity without electrical conductivity.

### 3.2.1 Market perspective: graphene/2D materials in composites

Solutions, where graphene materials can enter the market are currently mostly addressed by carbon composites. Figure 29 summarizes the global carbon composites market by applications in 2014. Expected yearly growth rates are 10.6%, resulting in carbon composites revenues of 33.6 Billion US\$ in 2021. [130]

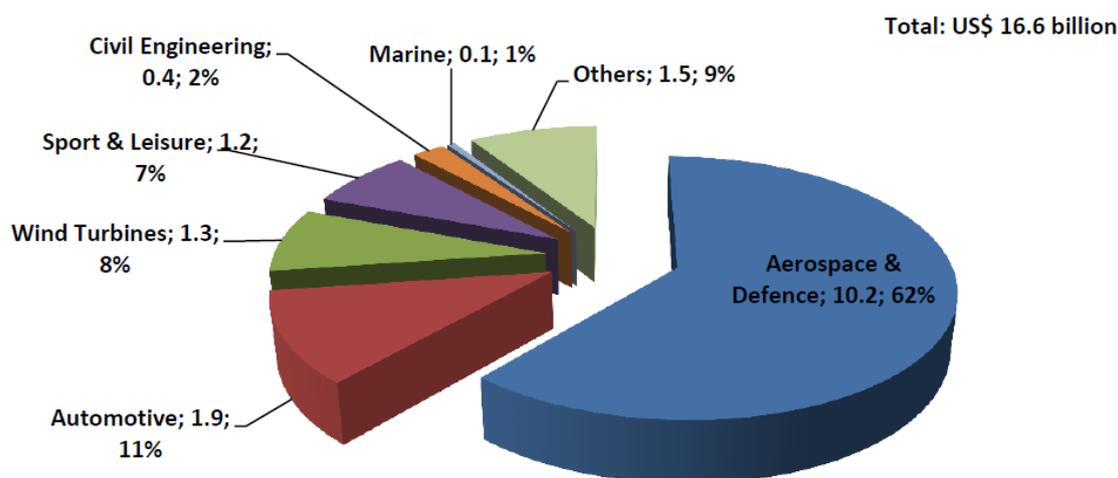


Figure 29: Total global revenues for carbon composites in 2014 were 16,6 Billion US\$, of which CRP (Carbon fibre reinforced plastics) accounted for 10,6 Billion US\$. [130]

Looking at the wider picture of the composites market in general, global market size in terms of value of end products is expected to reach around \$90 billion in 2020 with a CAGR of 7% to 9% between 2015 and 2020. [131] The market for lightweight materials was estimated to be between \$88 and \$116 billion in 2014 and is expected to grow to \$144-188 billion with a CAGR of 8% to 12% until 2020. [132, 133] Looking at high performance polymers in the transport sector, the market is expected to grow by ~5% per year in Europe and North America (2014: \$761m).

The functional composites market is still emerging; most of the composites nowadays used are for mechanical strength and low weight. The wider defined conductive polymers market for example is still juvenile and accounts for \$3-4 billion by 2020, where filled conductive plastic generates the maximum revenue, contributing more than 4/5 to the conductive polymer market, due to its extensive application in ESD and electromagnetic interference (EMI) [134, 135].

The advanced functional composites market including thermally/electrically conductive/resistive, barrier, optical magnetic and other functional composites was estimated to be \$41 billion in 2015 growing at a CAGR of 7.3% to \$58.5 billion in 2020. Main markets are in Asia-Pacific (47%), North America (25%) and Europe (19%). Major end users are consumer goods and electronics (25%), building, construction, storage and pipeline (23%) and transportation (22%). Main functionalities are thermal (29%), electrical (23%) and barrier (19%). [136]

Major trends served by these applications are for instance (functional, hybrid) lightweight construction, multi-functionality or 3D printing.

In terms of patents, polymer composites are dominating materials where graphene and 2D materials are used followed by metals, ceramics and concrete, see Table 9. The

number of graphene/2D material related patents increased over-proportional to the overall area, which can be seen in an increased share of graphene/2D related patents compared to the overall amount of patents in the respective field.

In terms of country distributions (Figure 30), the largest transnational patent activities are found in USA followed by Europe. Europe is particularly strong in polymer composites with graphene/2D materials.

Table 9: Patent analysis of graphene/2D materials in different matrices: Number of graphene related transnational patents in the respective fields in 2009-2011 and 2012-2014. The share gives the ratio of graphene patents from all patents in the area (0.8% of all ceramics patents dealt with graphene/2D materials in 2009-2011).[137]

Composites	2009-11	Share %	2012-14 <sup>g</sup>	Share %
Ceramics	107	0.8	235	1.7
Polymers	580	0.9	1155	1.7
Metal	147	1.2	322	2.4
Concrete			20 <sup>h</sup>	

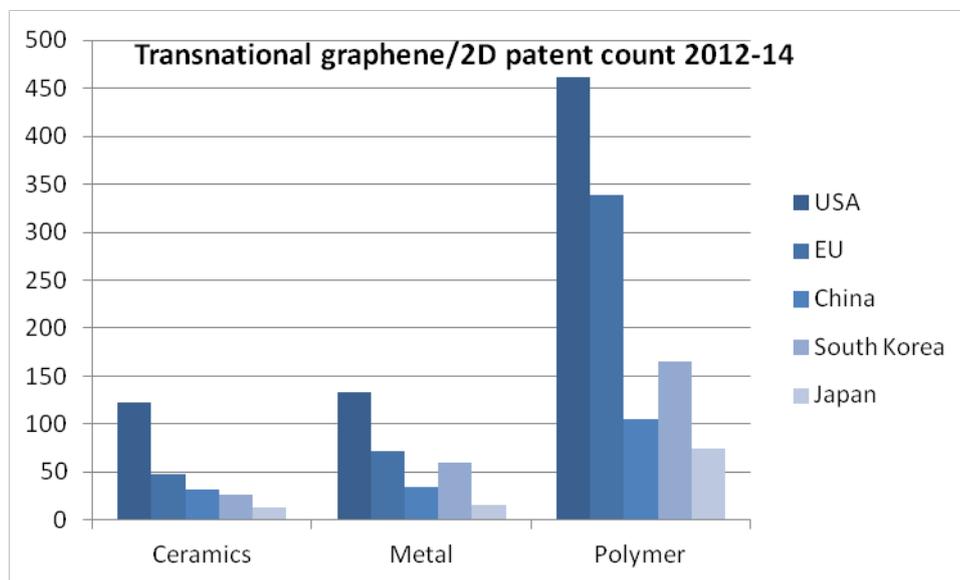


Figure 30: Transnational patent count in the respective area in 2012-2014 for different work regions. 2014 values are projected.[137]

<sup>g</sup> 2014 values are projected

<sup>h</sup> Values from 2009-2014

Looking at graphene polymer composites, Europe is second in terms of the transnational patent count after the USA (Figure 31). The relevance of graphene materials, however, is stronger in Korea and China (Figure 32).

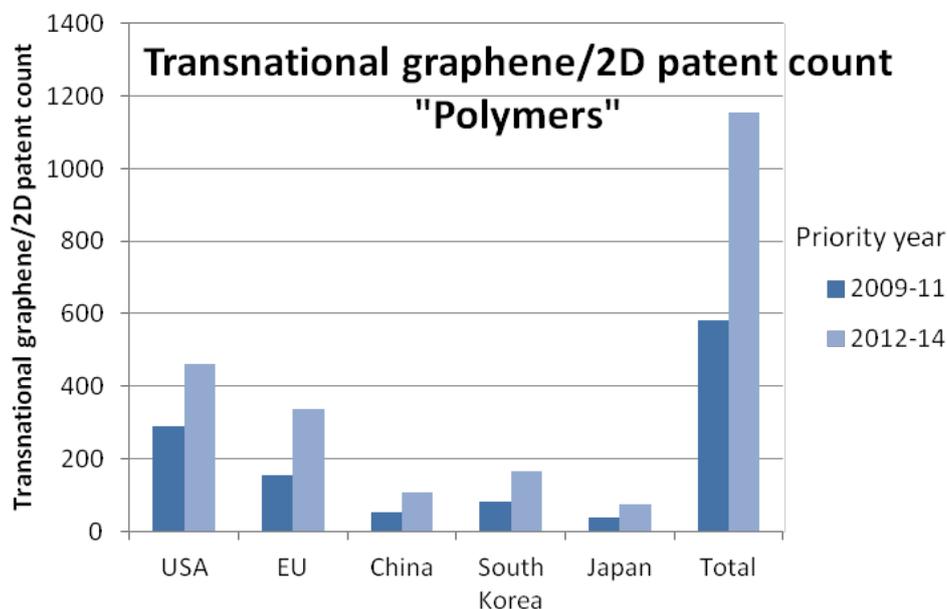


Figure 31: Patent analysis of graphene/2D materials in polymers: Number of graphene related transnational patents in 2009-2011 and 2012-2014. 2012-2014 values are projected. [137]

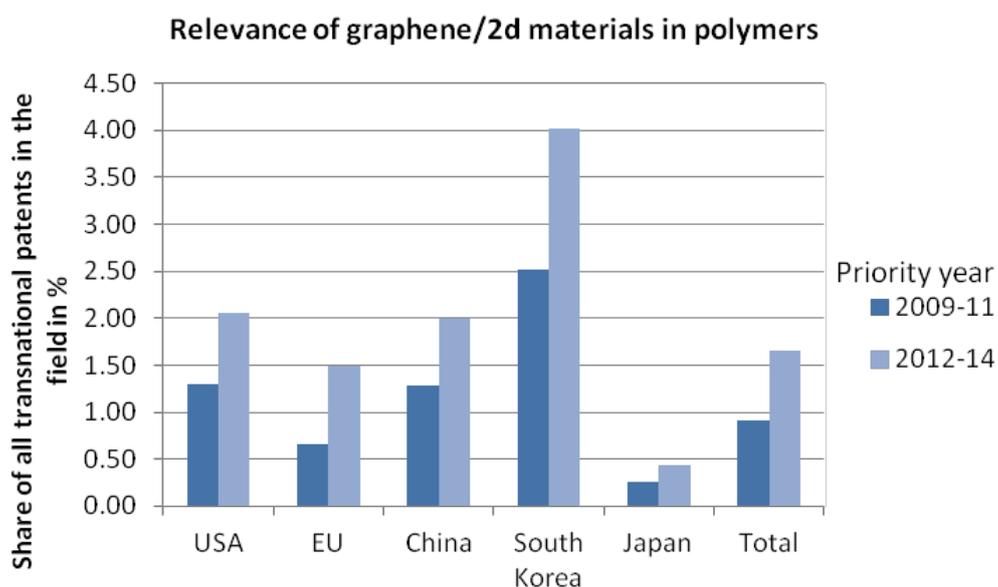


Figure 32: Patent share of graphene/2D related materials with respect to all transnational patents in polymers. 2012-2014 values are projected.[137]

Figure 33 compares the turnover share (worldwide) from EU-28, East Asia and North America for advanced materials and nanotechnology. For advanced materials, Europe is positioned between North America and East Asia, generating roughly a third of all turnover worldwide. In nanotechnology the picture is similar, although North America and Europe are similarly strong behind East Asia.

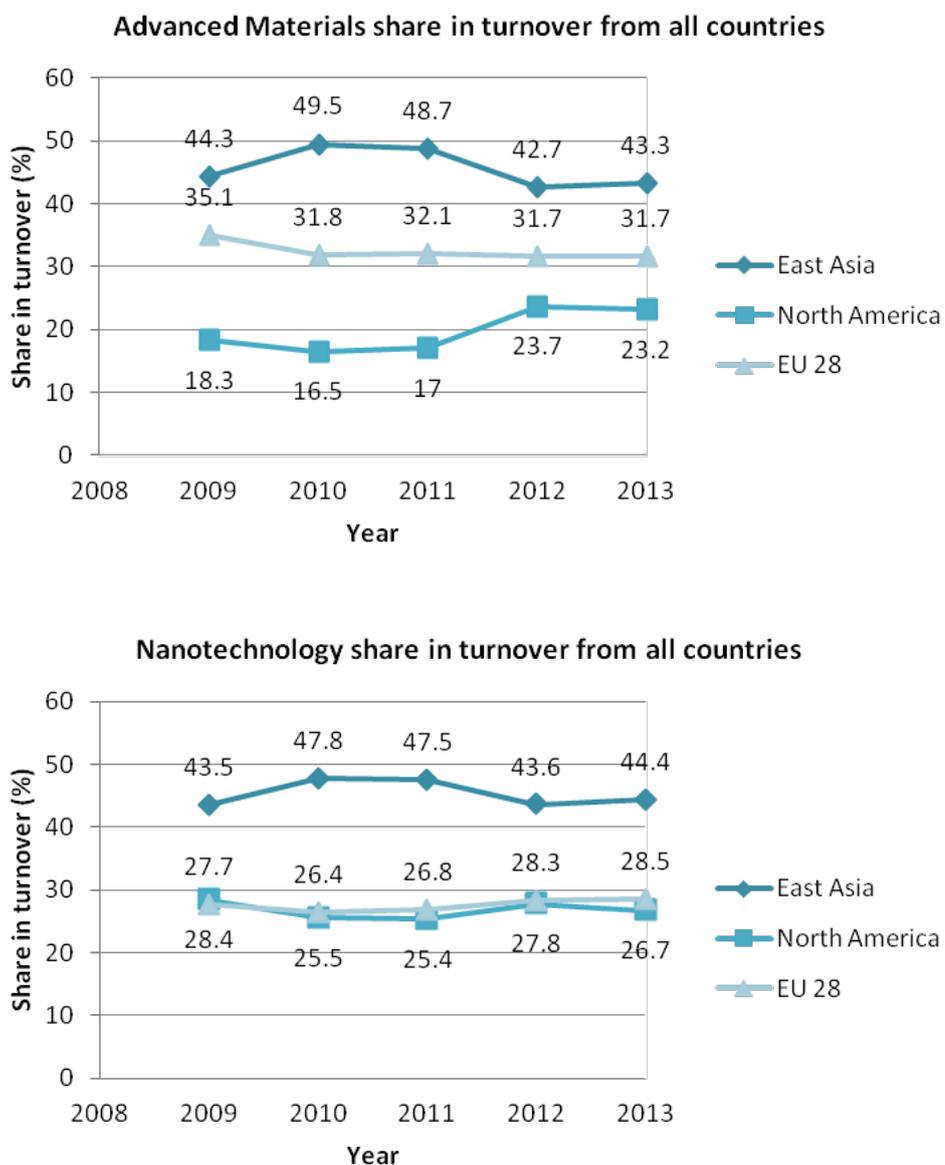


Figure 33: Share in turnover relative to all countries of advanced materials and nanotechnology. [138, 139]

### **3.2.1.1 Market Opportunities**

#### **3.2.1.1.1 European adopters and multiplicity of addressable markets**

As composite materials have a great variety and multiple applications, graphene enhanced composites can address, large, growing and strong (European) markets (automotive, aerospace, medical technologies, wind energy, energy transmission, advanced textiles, defence, packaging), compare also Figure 29, Figure 30 and Figure 34. These markets are very versatile and offer many niches and potential early adopters for an early market introduction. Some niche applications also allow higher costs for multi-functionality or increased performances, such as space applications.

Besides, graphene/2D materials enhanced composites address emerging topics such as 3D printing (e.g. conductive 3D printed polymers) or functional textiles. A benefit is that the materials sectors addressed by graphene fillers, such as polymers, are used to working with carbon materials as fillers (e.g. carbon black).

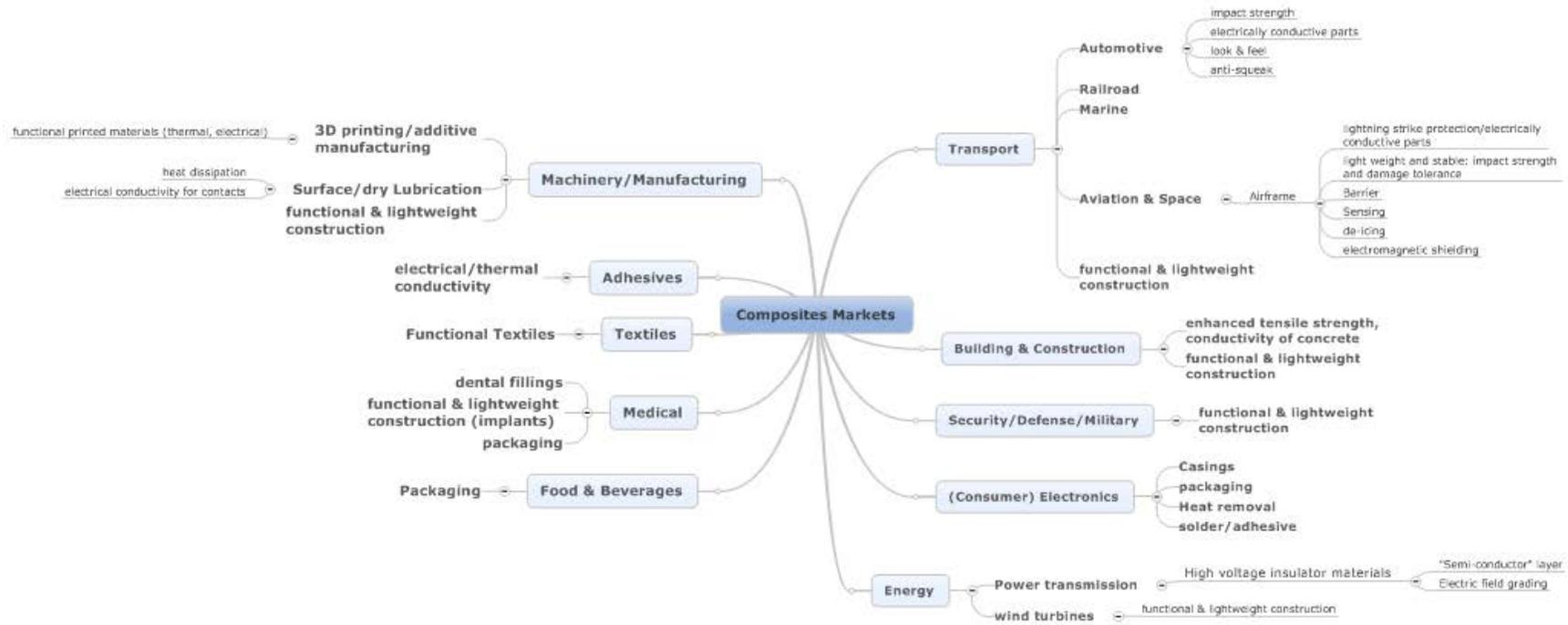


Figure 34: List of potential markets of graphene enhanced composites.

### 3.2.1.1.2 Trend towards lightweight/functional construction and increasing use of composites in relevant markets

Due to CO<sub>2</sub> reduction efforts, need for improved energy efficiency and regulation, especially in transport related sectors the demand for lightweight and functional construction is high. This trend creates demands for affordable lightweight material solutions and functional integration which maintain and improve strength and safety standards.

It is to a certain extent feasible to increase the cost for a given saved weight (cost/benefit). Estimates of this KPI is given in Table 10. Therefore, although the cost is usually increased when lightweight materials are used, the use of lightweight materials is expected to grow across industries. [140]

Table 10: Allowed added costs per kg saved in most relevant sectors.

Sector	Allowed added cost per kg saved (roughly)
Automotive	<3€ (mass market) -8€ (premium market)
Aviation	Few 100€ (depending on aircraft)
Space	Few 1000€ to 10000€

Polymer-based materials and composites are the main type of material used to address lightweighting, where graphene materials can play a role. In the automotive sector, polymer composites are expected to be preferred material by 2030 [141]. This not only accounts for structural components, but also lots of smaller components (e.g. where PEEK is used) in non-structural/non-critical components.

Wind power and aerospace are pioneering the use of novel lightweight materials. In aviation, composites are increasingly used in airplanes (wing and fuselage recommendation by IATA [142], Airbus A350XWB, Boeing 787 Dreamliner) to reach CO<sub>2</sub> reduction goals.

An interesting route to address the cost reduction in composites is to upgrade a low cost polymer by additives to facilitate use of a lower cost matrix for applications where currently higher cost resins/base materials are used. For instance, a bottleneck is the production cost of often used thermoset (epoxy based) reinforced composites due to the cost of structural epoxy resins and also the fibres. Advantages of thermoplastic reinforced composites are the easy processability and the decrease in production cost. Conventional thermoplastics have not achieved the mechanical performance of structural thermosets, which can be addressed by adding graphene materials.

In particular the mechanical enhancement can address interesting needs of several industries such as for example:

- enable lighter materials with similar strength and cost (all)
- Use simpler to process composites with similar performance: Use short fibres and injection moulding (all)
- Replace metals with composites (all)
- increase the mechanical strength i.e. impact performance and toughening of impact absorbing components (aerospace, automotive) for vehicle safety and crashworthiness
- Higher flexibility/elasticity of composites
- Better mechanics at elevated temperatures (or at extremely low temperatures) to extend the temperature window for use of a given material and avoid use of a much more expensive material

Typical early adopters in the sports industry have already taken up graphene materials in their products, see chapter 3.2.4.1 Current Maturity: First niche products are in the market.

Besides, European regulatory laws and agreements require recyclability of materials (e.g. components of vehicles; End of life Vehicle Directive). Important parameters are therefore also regarding the life cycle of composites and their reuse and recycling. One of the bottle necks for the use of thermoset composites in automotive industry is the difficulties of recycling, the best option being waste materials in the cement industry (in the cement kiln route) or just pyrolysis. The use of thermoplastic instead of thermoset materials can be an alternative due to the well stabilised recycling routes.

### **3.2.1.1.3 Demand for integrated (multi-)functional/smart materials**

Functional composites combine various properties in a single material, which allows lightweighting and functionality integration. In particular for this functional integration (functional lightweight construction, hybrid lightweight construction) [143] graphene based additives can play an important role due to their multi-functionality (electrical, thermal conductivity, mechanical reinforcement, barrier properties, anti-friction, flame retardancy).

There is a trend towards this functional integration [144] and multifunctional/smart materials, although actual applications are still not yet widely commercially applied, besides electrical conductivity or barriers to some extent. Therefore, it is expected that the use of functional polymers or other functional lightweight materials will increase in the next years.

In terms of multifunctionality for concrete or cement, the market chances need to be investigated and the market needs to be created/triggered, as there is currently hardly a market for a more conductive concrete or thermally enhanced concrete. The building industry is also very price sensitive and large amounts are needed, even if the loading is low.

The loading of additives to reach multifunctionality is often rather high, which leads to higher cost, different processes and cross-correlation with other properties, such as mechanical strength. A graphene material opportunity is that usually rather low loadings are needed to achieve desired effects.

#### **3.2.1.1.4 3D printing and additive manufacturing as driver**

In particular for polymer based 3D printing, 2D material additives can play an enabling role for functional plastics (filaments, photopolymers, e.g. with higher strength or thermal/electrical conductivity). Graphene/2d materials can benefit from the strong growth in this sector (20-30% for consumables [145], ~10% for the 3D printing market [146]). Besides, currently rather large premiums can be charged for 3D printing materials, which reduces the barrier for integration.

#### **3.2.1.1.5 Opportunities in metals and ceramics**

Besides the use as coating for metals (see for instance 3.3), also metal and ceramics composites are interesting areas as host material. Both European industries have a large worldwide market share (see 3.2.1.1.8). The worldwide advanced functional composites market is estimated to be \$83 billion in 2015, growing at a solid CAGR of 5% in the next 5 years. [136] The metal matrix composites market was estimated at ~\$320 million in 2015 growing at a CAGR of 6% in the next 5 years. [147]

Metal matrix composites are used to enhance functionalities, improve certain properties (electrical, thermal) whilst reducing weight, e.g. increased strength of aluminium for transport applications, improve metals for electrical applications such as batteries or supercapacitors or improve the corrosion resistance. Challenges of this technology are high manufacturing costs and limited technological expertise. [148]

Ceramic materials have very valuable properties from the engineering point of view, such as refractoriness (i.e. retaining material strength at  $T > 600$  °C), strength and hardness, but they have an important drawback, their low toughness, which often overcomes their potential benefits. The usual approach to increase toughness is the inclusion of second phase materials that may act as reinforcing agents by producing extrinsic toughening effects. This agent could be nano-additives such as carbon fibres, carbon nanotubes and graphene. An additional benefit to add such additives is to render the ceramic composites electrically conductive, which is also interesting for better machining possibilities (see 3.2.1.2.1).

### **3.2.1.1.6 Interest for trials from industry**

In principle, there is interest in graphene/2D materials in composites and coatings from application industries (e.g. aerospace, automotive, chemical industry, electrical and electronics, construction, defence). Customers/end users demand prepregs, thermoplastics, resin dispersion in paints and thermosets with graphene for testing, so the interest for trials is there.

As for example CNTs are more mature, there might be also synergies/boosting with other (carbon) materials or nano-additives.

In particular when it is not needed to change the production technology, the introduction of a new material can be straight forward and rather easy. For that reason the use of pre-dispersions in solid, liquids or polymers used as nano-intermediates (GRM dispersion in solids for the rubber industry, masterbatch for the thermoplastic industry and prepegs or resin dispersions for thermosets) for test and development of graphene-enabled final products is the way forward, that is also pursued by many suppliers.

### **3.2.1.1.7 Health concerns about CNT**

Occupational health concerns about CNTs are considerably bigger than about graphene. Providing reliable answers that graphene is less problematic than CNT may help graphene to win in applications for which CNTs are presently leading candidates under consideration.

### **3.2.1.1.8 European value/supply chain**

Europe also plays a major role in terms of industrial production of composites or materials. Potential integrators of graphene additives (compound, prepreg, masterbatch producers) are located in Europe. For instance, Europe is the second largest plastics producer after China (20% vs. 26%) with a positive trade balance and a turnover of 350bn€. [149] In 2013, a total global revenue of \$14.7 billion was created with carbon composites, of which 34% were generated by US companies and 32% in Europe, followed by Japan (15%) and Asia & Pacific (13%). [150] Furthermore, the demand for carbon composites is also strong in Europe, see Figure 35. Besides, Europe is also rather strong in the patenting of graphene and related transnational patents, especially in the polymer composites area, but also in ceramics, compare Figure 30.

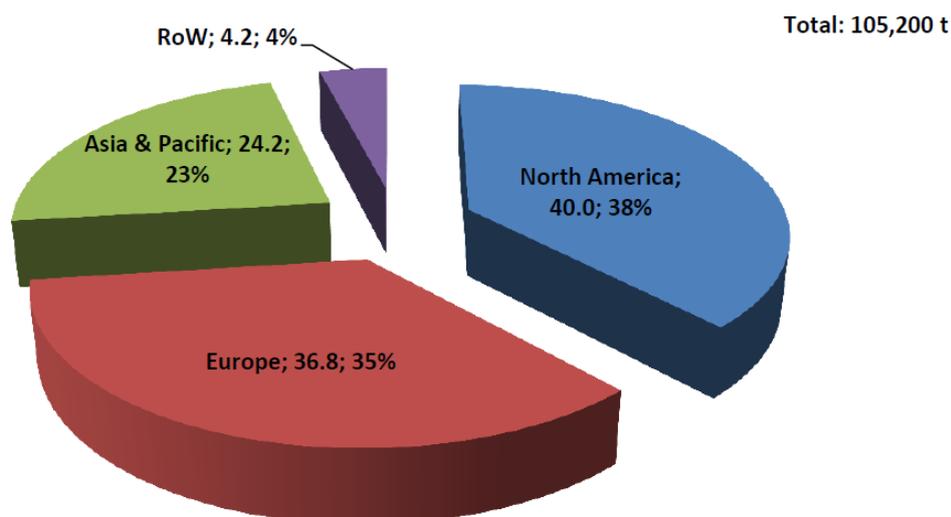


Figure 35: Carbon composites demand in 1,000 tonnes by region (2014). [130]

It is important to involve the prepreg and compound actors in the integration of graphene (e.g. Delta Tech is in the Graphene flagship or Haydale collaborates with SHD Composites Limited [151]). For a broader integration, these collaborations need to be enhanced, see 0., also to figure out whether additional steps are needed in the value chain

The European ceramics industry produced revenues of ~€27 billion in 2014 with a positive trade balance and 25% of global production [152]. The steel industry is the second largest in the world with an output of over 177 million tonnes of steel a year, accounting for 11% of global output. [153] Both industries are under pressure from worldwide competition.

The annual total added value of the European cement and concrete industry was €56 billion in 2013. [154] The production value of ready mixed concrete was 16.1b€ in 2014. [155]

Furthermore, Europe is a naturally strong player in terms of patenting and innovation in the polymer industry. Figure 36 shows that Europe dominates the number of transnational patents dealing with polymers together with the US. It is equally strong in ceramics and metal composites.

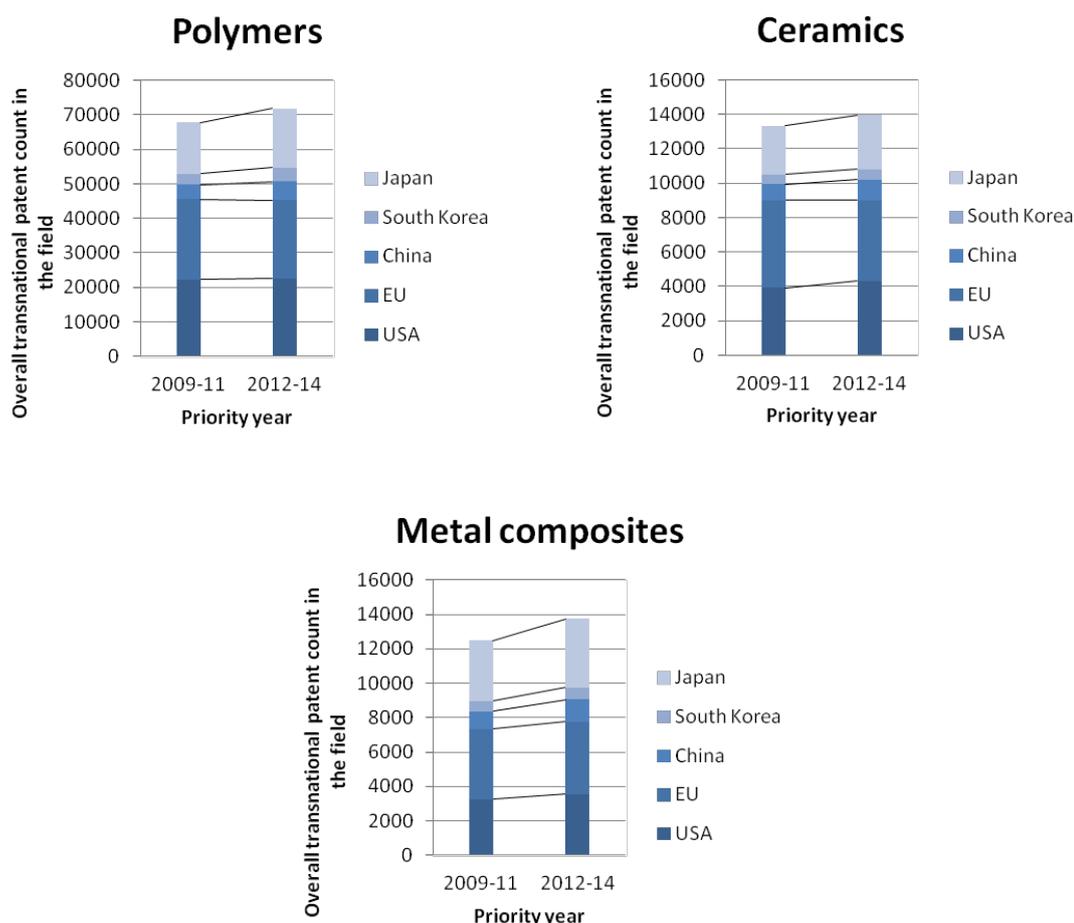


Figure 36: Overall transnational patent count in polymers, ceramics and metal composites. 2012-2014 values are projected.[137]

### 3.2.1.2 Additional market opportunities: conductivity

#### 3.2.1.2.1 Electrically conductive composites on the rise

Chapter 4 highlights the interest for multifunctional/smart materials. Besides the mechanical enhancement, conductivity is an important need from industry for these multifunctional materials and probably already the most pursued approach, as several companies are active in that respect (also with other technologies than graphene):

- Anti-statics, electro-static discharge (ESD)
- allow lighter EMI (electro-magnetic interference) shielding
- lightning strike protection (aerospace)
- functional integration of signal transmission/sensing in lightweight structural parts, i.e. wiring within plastics (automotive, aerospace), e.g. for entertainment in airplanes
- lightweight electrical heating elements (e.g. automotive, de-icing of airplanes)
- electric field (electric stress) grading material in insulation systems for transmission and distribution of power (see box on page 118)

The electrical conductive composites and conductive polymers market is expected to grow with a CAGR of ~8% annually. The overall market of electrically conductive composites is expected to grow at a similar rate.

For ceramics, conductivity can enhance the possibilities of machining by more efficient methods, such as electro-discharge. This benefits from the erosive effect of electrical discharges or sparks (usually ceramic materials are costly to machine into complex shapes).

An ultimate vision would be to achieve a carbon-based lightweight conductor, which might be suitable for particular applications where light weight and corrosion resistance is more important than ultimately high conductivity.

#### **3.2.1.2.2 Harsh environments as interesting opportunities**

Electrical conductivity is usually reached by using metal additives. However, in corrosive and harsh environments or hot conditions metals can degrade or use their mechanical properties. These areas are rather niches, but still have a certain demand for corrosion resistant conductive materials.

#### **3.2.1.3 Additional market opportunities: thermal properties**

##### **3.2.1.3.1 Need for passive and energy efficient cooling or heating**

Similar to the electric conductivity, thermal properties are also important to be integrated into multifunctional composites. Composites can be used to remove or spread heat better than usual polymer materials. Directionality can additionally help to improve the thermal performance. The market for thermally enhanced composites is expected to grow with a CAGR of almost 8.5% in the coming 5 years. [136]

Thermal interface materials are further investigated in chapter 3.3.

### **3.2.1.4 Additional market opportunities: barrier properties**

#### **3.2.1.4.1 Water barrier in epoxy resins**

Carbon-fibre reinforced composites can suffer from water uptake of the epoxy resin [156]. Additives can help to improve the water barrier and prevent fatigue and at the same time achieve other properties, such as flame retardancy.

#### **3.2.1.4.2 Many potential applications in packaging**

Barrier properties are important in many different areas, e.g. in semiconductor, fuel tanks, gas storage, food packaging, beverages and medical applications. These applications are nowadays addressed by multi-layer structures or coatings. Adding a barrier within the primary material/host could simplify the processing.

For food, beverages and medical applications the regulatory (health and safety) constraints are, however, larger than for the other applications.

The use of ESD and conductive films for electronics packaging will increase in the next years. However the use of conductive carbon blacks and CNT are not suitable technologies, due to the rheology and MFI change in the polymer. Still other options are also competing on the market based on other antistatic agents, metal films or conductive polymers.

The market for composites with barrier properties or electrical properties/conductive polymers is expected to grow with a CAGR of around 7% in the next 5 years. Conductive polymers had an estimated world market of ~\$3 billion, barrier composites of ~\$7.4 billion in 2015. [136]

#### **3.2.1.4.3 Opportunities for flame retardancy in polymers**

More restrictive regulatory standards of the European cable industry are emerging, that will be also adopted in China. ATH and MDH filler polymers have difficulties to obtain the requirements, which opens opportunities for new flame retardant additives. Also the tendency of restriction of use of ammonium polyphosphates will be a new opportunity for graphene materials.

Besides, most used flame retarding additives use rather high loadings (20-60%), which can affect properties such as mechanical stability, so that adoption to each polymer is needed, This also has an impact on cost (see 3.2.1.6.2).

### **3.2.1.5 Market Threats**

#### **3.2.1.5.1 Mature markets with many established technologies and complex value chains**

Some of the markets targeted by graphene/2D material enhanced composites are already very mature. Additives to all kind of hosts (polymers, ceramics, concrete, etc.) are a mature and well established market. There are also nano-additives addressing similar (separate) enhancements as graphene, such as CNT or nanoparticles of many different materials. In particular for barriers, thermal or structural enhancements, many additives are under investigation. However, the multifunctionality of graphene materials as an additive is rather unique.

In terms of CFRP, the market is still rising and the majority of fibre composites used at the moment is glass fibre based, in particular in the automotive industry (automotive: 93.2% GFRP in 2014). But the CFRP share is expected to increase and the revenue of CFRP is expected to grow globally by CAGR 21% for the automotive industry. Already the introduction of CFRP requires a completely different supply chain compared to metal-based structural components. The current key focus of CFRP manufacturers is the cost reduction. [157] If this can be addressed by graphene, it can be a great opportunity. This could for instance be the case if thermoplastics instead of thermosets can be used while achieving the same properties for lower material and process cost. If costs are increased through graphene usage, it is a threat.

In terms of other nano-additives, one of the main competing materials are CNTs. They are already more mature and better understood (because they are longer studied). So far there is no large roll-out, but it appears that some composites are about to be used for similar applications than graphene. A clear advantage is therefore necessary towards competing technologies. The market is in general very competitive and thus it is hard for a new material to enter the market and outplay competing technologies, even if performance is slightly better. But in case this is successful, a market success can be large, as scaling is usually targeted and desired.

Also graphite powder has interesting properties that might be sufficient for less demanding applications, especially in terms of conductivity. They currently can be obtained much cheaper (0.8€/kg at industrial quantities). However the quality and size covers a broad range (from 200nm to several microns).

Flame retardant additives (even halogen-free) are already known and widely used, however, the halogen and antimony-flame retardant solutions often demand high loading.

In terms of conductivity enhancement, carbon black works quite well for some applications demanding lower conductivities, however, in medium high and high electrical conductivity, conductive carbon blacks are not suitable due to high increase in viscosity of

the resin or the thermoplastic. Another drawback of conductive carbon blacks is the brittleness of the composite due to the high loading. But clear advantages need to be proven to replace existing and working conductive additives. For antistatics (e.g. spark protection), which demand rather low conductivities, even more solutions are available so a clear differentiator is needed. On the other hand, most of the antistatic solutions are based on the migration of molecules to the surface of the matrix, rendering it a non-permanent antistatic material. A potential differentiator could be added functionality or low amounts of needed additive.

The composites address complex markets with complex and established value chains with many stakeholders (compounds, master batches..., compare Figure 37). Getting access to these value chains remains a large barrier, especially because they are quite conservative. Depending on the actual target market, these can be very cost sensitive. Due to the variety of potential applications, it demands great efforts to find the right markets and address and prove the needed performances.

There are also strong constraints on the sourcing of materials. Usually a second source/supplier is needed that offers the same quality and standardized testing and quality control are very important.

Last but not least, only if a material can be integrated easily into the existing production processes, a quick uptake is possible. If new equipment is needed, the benefit needs to be much larger and the implementation will take much longer, if it is considered at all.

### **3.2.1.5.2 Large markets have restrictive requirements on cost, function, health, safety and end of life**

Large markets are cost sensitive markets (e.g. automotive), but legislation is a driver to use also more expensive materials. In aeronautical market cost is also becoming a key driver for future aircraft developments. A cost/benefit analysis needs to take into account the system cost and the life cycle cost, which can in some cases justify the initially higher investment for composite parts. However, quite often only immediate costs are recognized and not total system costs. But the total system costs might actually be reduced by adding multifunctionality: Although adding conductivity or thermal sensing to the composite might be more expensive initially, money can be saved in the later process by eliminating the need for a separate system. [158]

However, in the mass markets, composites are at the moment not yet widely used as they are still to a great extent cost prohibitive. In the automotive industry, polymer based composites for structural applications are still not broadly used and mostly reserved for high price luxury segments. Mass markets lightweight strategies are still dominated by cheaper high-strength steels, aluminium or other lightweight metals, partially combined with carbon-fibre or polymer based compounds. [140] Added costs through higher priced materials are still often contrary to many strategies (e.g. in automotive). In almost all

potential applications of lightweight materials, cost is still the highest barrier [143]. But aviation and space applications are not so cost prohibitive, so that the integration of higher valued materials is easier.

For CFRP, the current costs are 100€/kg, of which about 1/5 are for materials. So the limiting factor is the processing cost of 4/5. Thus, the highest cost reduction potential comes from the processing and not from the materials. It is therefore unclear how graphene materials can actually contribute effectively to a cost reduction.

The building industry is very price sensitive. The price of concrete is \$85-100 per metric tonne, which can limit bulk graphene applications even at low loads. Also the low cost of other building industry materials, for example, ceramic bricks with a medium price of 50 €/m<sup>3</sup> can be a bottle neck. On the other hand, the markets are large (e.g. the flooring market is expected to be 300b€ in 2020. [159]

However, cost is not the only barrier that needs to be overcome or taken into account. There are also many requirements such as health & safety, durability and recyclability that need to be proven before a material can actually be used.

For example, the sustainability and recycling of composites is a major issue for the automotive industry and end of life considerations are essential for graphene materials. Recyclability/biodegradability and influence on life cycle of matrix can thus be a threat but also an opportunity, if it is shown. Anyhow, it needs to be addressed. In terms of durability, standard tests need to be performed (accelerated testing).

Health and safety considerations are particularly needed for the manufacturing and for release in crashes or during recycling. For food and medical applications, the constraints are even higher.

In all cases, just improving the properties of a given material is less relevant for industry; rather the improvement must be achieved at lower cost or other advantages relative to other, already existing materials.

### **3.2.1.5.3 Awareness and perception of graphene additives**

Often nano-carbon additives are not yet on roadmaps (e.g. IATA) or not recognized in market driven (composites) communities. These communities still have a rather observational attitude and do not get engaged heavily. The current situation is still strongly technology push oriented from the graphene community.

Graphene as an additive to composites is often seen in analogy with CNT. For CNT mechanical, electrical and thermal property enhancements were also shown [160]. For CNT composites the mechanical topic was very prominent at the beginning but shifted

more and more to functional properties/enhancements. In comparison with CNT, graphene has several advantages, such as its easier synthesis (no metal catalyst, lower temperature) and better dispersibility.

With respect to the perception of graphene materials, they are quite often compared to CNT with a negative undertone [161]. A problem are the high expectations (stronger than steel, more conductive than copper), that without being properly put into perspective lead to high expectations that will not be fulfilled with composites. Therefore, an honest advertisement is needed to education end users to manage the expectations and highlight the application related actual benefits.

Although the health and safety concerns might be not critical from a scientific point of view, the perception of safety issues in the broader public is also a major barrier and concern (“asbestos” analogy). Therefore, a clear proof and an open discussion is needed.

### **3.2.1.6 Additional market threats: barrier properties**

#### **3.2.1.6.1 Usually rather low cost products**

The composites/plastics mass markets demand low cost additives. In particular for the large packaging markets, low cost is a prerequisite, as the products are mostly disposable. Competing technologies are also promising: zeolites, silica or polymers.

#### **3.2.1.6.2 Additional market threats: flame retardant properties**

In terms of flame retardancy, the most important issues for polymers are solved (FST: flammability, smoke, toxicity with halogen-free additives). There are several additives available that work well with base level polymers (e.g. TFP Tris(2,2,2-trifluoroethyl)phosphate), ATH Aluminium Trihydrate, MDH Magnesium Hydroxide). Exfoliated graphite is already used and the performance is good as it decreases movement of polymeric chains. However, the loadings for certain polymer compounds need to be high to reach a reasonable flame retardancy (often above 55%), which in turn reduces the mechanical stability. This provides an opportunity for graphene materials as additive (see 3.2.2.1.3, high BET graphene has proven to be interesting) or coating (see 3.3.6).

In order to be feasible for flame retardancy, the FST test standards of particular applications have to be met (e.g. for airplane interiors, trains, automotive, cable industry). If not via cost or much better performance, graphene or 2D materials have the best chances to enter the market via the multifunctional enhancement, where the flame retardancy is combined with other interesting properties, such as increased strength, electrical and thermal conductivity and/or self-sensing of fire damage.

In terms of cost competition, the average price of a flame retardant additive is \$2.1/kg and loadings are up to or even higher than 55% by weight. For lower percentage of feeding, high performance polyphosphates are the alternative in halogen and antimony free flame retardant materials, however, the price of these materials is 4.0 to 7.2 €/kg with loadings of 35% or 20%, respectively. The overall market for these additives was \$2.07b in 2014 in North America and Europe with a projected CAGR 4.4% in revenue (Europe only: \$1.07b revenue and CAGR 3.7%, being ~10% of the European polymer additives market of \$13b). The demand stems from building and construction, electrical and electronics, automotive, and wires and cables industries. [162]

### **3.2.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in composites**

#### **3.2.2.1 Current strengths for graphene/2D materials use in composites**

##### **3.2.2.1.1 Multi-functional property enhancement of host material and improvement potential**

The unique selling proposition of graphene materials as an additive in composites is its multi-functional property enhancement. By adding graphene one can not only address a single property such as mechanical enhancement, but also at the same time electrical and thermal conductivity, barrier properties, chemical inertness etc. Also added functionalities such as self-healing capabilities of elastomers can be triggered by graphene materials, which is currently investigated. The presence of graphene materials also allows self-monitoring and self-repair in thermoplastic composites (by the Joule effect), or simple sensing, due to their electrical conductivity.

With these property enhancements, graphene and other 2D materials address common composite challenges of stiffness, strength, fatigue, improvement of crash and impact resistance, environmental resistance, creep, energy management or temperature capability. Ultimately, the functional enhancement can lead to added functionalities such as sensing capabilities or for damage detection. The chemical inertness allows usage in corrosive and harmful environments (sea, chemical plants). It has also a tuneable transparency or absorbance to certain wavelengths of the electromagnetic spectrum (e.g. radar, UV or infra red light) and can thus potentially be used to adjust the interaction of the host material with electromagnetic waves. On top of that, graphene has a potential end of life strengths: it is a carbon based materials, where recyclability, biodegradability or residue-free combustion capability is possible, but clearly needs to be proven. Graphene might not be necessarily better than other technologies for the single parameter enhancements, but the combination is unique. This multi-functionality opens possibilities for new design of components due to integrated functionality and increased strength.

The theoretically high performance improvement potential for these properties is encouraging. Although graphene materials will hardly improve the properties of the host material to the level of pristine monolayer graphene, there is still a large gain possible and room for improvement (see Figure 27). Many potential improvements are shown in the lab (mostly for singular parameters). These “flashes of positivity” now need to be further elaborated to actually prove the benefit in functional environments and the economical feasibility.

Another potential business case is the upgrading of cheap host materials (e.g. polymers PP, PE or chopped fibre-reinforced polymers, using thermoplastic instead of thermosets in structural CFRP) to allow usage in other applications where higher performance is needed for a lower cost. This in turn could enable use of simpler production methods (e.g. use of injection molding/infusion for short-fiber CFRP). In particular for this application it is important to consider the appropriate competing materials i.e. making a cheap polymer better will only be relevant if the improved polymer comes at a price that is lower than that of another material that achieves the properties of concern already without improvement.

While most of the research work has been concentrated on composites of graphene with a polymer matrix, promising results have been obtained more recently also for metal matrix composites (MMC) and ceramic matrix composites (CMC). In literature, only limited researches on metal matrix composites reinforced by graphene are available. Graphene and carbon nanotubes (if processed in the correct way) can give structural reinforcement and self-lubricating properties to metals, influencing as well their microcrystalline structure and reducing the density of the material. [125] In ceramics, better strength and lower brittleness as well as increased conductivity are investigated. [127] Also functional enhancements, for instance for battery electrode, supercapacitors, corrosion or sensing are possible. [126]

### **3.2.2.1.2 Influence on electrical/thermal conductivity of host**

Besides the mechanical enhancement and the multi-functionality, graphene materials are especially promising to improve thermal and electrical conductivity of the host material, which allows “functional lightweighting”.

Carbon black and graphite are already widely used to introduce electrical conductivity, e.g. in ceramics or plastics. However, using graphene materials increases the conductivity further, allowing additional applications to be addressed. For instance, aerographite-PDMS composites are investigated for de-icing purposes and show quite promising results. Further improvement of the conductivity of the composite and thus of its heating behaviour could be achieved by combining the aerographite network with graphene material.

Conducting composites with graphene material as additive are already on the market (e.g. for 3D printing)<sup>i</sup>.

Adding conductivity to a composite also allows additional "sensing" properties for degeneration or breakage. A particular strength is the corrosion resistance of graphene, allowing the use in harmful environments, where metals are degenerated. The tuneable transparency or absorbance to certain wavelengths of the electromagnetic spectrum allows also usage where metals are disadvantageous (e.g. for radar dome de-icing).

For conductive applications, graphene material yarns (similar to CNT yarns) could be used as carbon based conductor for electrical signal transmission. In that case graphene is used as a rather pure bulk material and not as an additive. The challenge in that case is to allow higher currents through bulk transport, which calls for a 3D architecture to increase the overall transported power and current. Carbon based power cable constructions, a very visionary application, are not yet possible with material available. However, in high voltage applications graphene materials can be used as the "semicon" in the insulation of power cables and as an electric field grading material both aiming at stress reduction of the insulator.

In case thermal conductivity is needed without electrical conductivity, graphene materials are not viable as the two properties cannot be separated. In that case two-dimensional BN can offer a solution, as it increases the thermal conductivity but is electrically insulating.

Use of low amounts/loading of graphene/2D materials to achieve a good conductivity/good properties might lead to cost advantages eventually.

### **3.2.2.1.3 Flame retardancy and gas barrier properties in polymers**

Graphene and other 2D materials can also increase flame retardancy in polymers. Exfoliated graphite is already used in this respect, and an increased thermal stability of polymers by several tens of degree centigrade were observed, reducing also the LOI (Limiting Oxygen Index).

The chemical stability and layered structure of 2D materials is beneficial for flame retardancy. There are synergistic effects with exfoliated graphite/other retardants to decrease movement of / immobilize the polymeric chains and improve anti-dripping and improving surface char generation as a protection: It has been observed that the use of high BET graphene materials allow to obtain better performance than with exfoliated graphite [163] and it also has synergies in combination with other flame retardant materials such as  $Mg(OH)_2$  and phosphates. [164] The flame retarding performance of graphene materials and the increase of the thermal stability of the polymers, even at low loading, and its

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<sup>i</sup> E.g. <http://www.graphene3dlab.com/s/home.asp>

synergetic effect with other low cost flame retardant materials such as ammonium mono-phosphates (<1€/kg) can allow to have a price competitive alternative to other halogen free flame retardant materials.

Graphene materials thus perform to a certain extent better than other carbon materials and business cases are identified (see paragraph above), but it is still under discussion and debated whether other flame retardants can be outperformed in terms of cost/benefit on large scale. It also needs to be considered that enhanced IR absorption brought into materials by graphene may counteract to an initial benefit due to additional heating. The use as a coating is also possible, which in turn does not affect the mechanical properties of the host at all (see 3.3).

Although most of the problems, such as avoiding the use of halides, antimony or borates are already solved for polymers, still high loadings or higher cost materials such as ammonium polyphosphates and ammonium polyphosphates combined with char promoters are needed. The average price of a flame retardant additive is \$2.1/kg for materials demanding high loading (55%) [162] and ~4-7€/kg for materials demanding lower loading (20-35%). In order to compete with that in terms of pricing, the loadings or the additive prices need to be low enough. Graphene materials benefit can be that a much lower loading is needed, which in turn does not change other properties (or even improves them).

Besides, graphene materials can add value when the multi-functionality is desired (e.g. increased strength, electrical and thermal properties).

However, smoke and toxicity need to be investigated for further implementation (application depended: there are differing regulations depending on the use in cars, trains or underground, aircrafts).

The commonly used flame retardant MDH Magnesium Hydroxide (unit shipment share in Europe of 9.2% of all flame retardant additives in 2014 [162]) is also available in a two-dimensional form. This modification could actually lead to improving the performance parameters or to reduce the needed loading of this additive.

Barrier properties can also be enhanced with graphene and other 2D materials, e.g. for gases. When they are well dispersed in the host material and have a reasonably large aspect ratio, the pathway for gases can be enhanced. Barrier properties of graphene nano-sheets are for instance approximately 25 to 130 times superior to those of clay nano-fillers at low concentrations. It remains to be seen how they compete with established coatings.

#### **3.2.2.1.4 Straight forward, scalable preparation, integration and processability for polymers**

A benefit for early adoption of graphene materials in composites is that very often multi-layered graphene, graphene nanoplatelets or graphite nanoflakes are sufficient to reach desired improvements. These bulk materials can be rather easily produced from metal-free, low-temperature and scalable wet exfoliation of graphite or reduction of graphene oxide, which is in contrast to carbon nanotubes, that are usually produced in vacuum or dry vapour processes by using catalysts.

There are also potential in-situ methods to produce graphene (e.g. exfoliation in a thermosetting polymer), however, these are currently not feasible due to open questions on how to achieve sufficient quality and control (e.g. distribution of lateral size)

The further integration in the host material is possible in various ways. It is essential for all applications to achieve a uniform dispersion of the added graphene/2D material. In polymers, it can be incorporated in the melt, by a masterbatch or prior to polymerization. Most importantly, the flakes need to be well dispersed.

Using additives in a masterbatch or prior to polymerization is more desirable, as the further processing of the composite requires no change in common standard production methods, i.e. there is no change in the downstream industry needed.

For ceramics it can be added as a powder in a wet mixing process, e.g. in colloidal solutions before sintering. For cement and concrete for example graphene oxide can be added during mixing.

All these processes allow the final composite to be further processed in a usual way, although the additive might influence the process characteristics of the composite (e.g. workability of concrete) positively or negatively. Dispersions or Predispersions of the material could help to further improve the processability.

#### **3.2.2.1.5 Resistance against corrosion and heat**

Graphene materials usually withstand high temperatures and corrosive environments due to the chemical inertness. So even if the performance such as mechanical strength or thermal conductivity does not reach certain levels, e.g. of metals, the potential use in these harsh environments and lower degradation can be the USP for particular niches.

#### **3.2.2.1.6 Relatively low implementation barrier in polymers**

Due to the somewhat simple integration and the use of graphene nanoplatelets and GO, the use of graphene and 2D materials in composites has a rather low implementation barrier compared to other potential applications. This is further supported by the rather

low loadings needed to get an effect. The latter of course depends on the application and host and typically varies from  $10^{-2}$  % to a few percent by weight.

This low implementation barrier has led to the fact that the (so far) only actually marketed applications of graphene materials can be found in the composites area, i.e. in sports equipment. The manufacturers use graphene or graphite platelets to improve the mechanical properties of the compound.

### 3.2.2.1.7 Value/supply chain for polymers emerging but still open questions

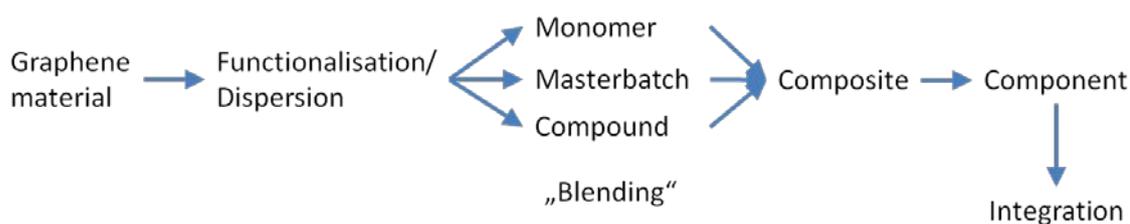


Figure 37: Simplified processing of polymer composites. The steps for other host materials are comparable with different processing techniques when it comes to composite preparation.

As mentioned in the prior subsection, the supply chain for 2D materials based composites presumably requires a change in the typical supply chain for composite materials, due to the low apparent density of the high BET graphene materials and in some case the functionalization (see Figure 37). There are several intermediary companies who specialize on this functionalization and predispersion, such as Haydale in the UK, if this is not done by graphene providers themselves (e.g. Avanzare in Spain or Angstrom Materials in USA, are producing predispersion and/or masterbatches for the reduction of steps in the graphene value chain).

Such intermediate companies or graphene suppliers dedicated to the introduction of the graphene materials in matrixes can sell ready to use masterbatches or pre-dispersions tailored to the correct employment of end users. They can also define working conditions with the prepared masterbatches, because for instance depending on the screw elements, it could be possible to break graphene sheets and lose properties.

Nonetheless, the supply chain is still in its infancy. There are companies of each step of the value chain in Europe and also the graphene material part is covered. Also in terms of the coverage of potential integrators, Europe is well situated (see 3.2.1.1.7).

One issue that is still persistent is the effectively/safe packaging and transport of graphene or 2D materials. This depends on the position in the value chain and is more of a concern for graphene material producers that do not integrate the material in a host (the composite/masterbatch/resin transport and packaging is not a problem). Especially for

global value chains this issue can be a problem how to ship tons of graphene materials as powders or dispersions safely and stable.

Massive applications are not competitive in price at the moment, but it is expected that the price of high performance graphene grades will decrease significantly in the next years. The optimization of formulas and performance together with the reduction in price might eventually lead to competitive graphene based materials.

### **3.2.2.2 Current weaknesses and challenges of graphene/2D materials use in composites**

#### **3.2.2.2.1 Variability of supply of graphene materials and missing standardization and knowledge of the needed quality of material**

Many different types of graphene are sold on the market for different prices. For composite applications the quality ranges from expensive single to few layer graphene flakes to multilayer flakes and cheap graphene nano platelets or nano-graphite (see Table 4) with different lateral sizes and oxygen contents. The lack of standardization and certification leads to the problem that all these very different materials in terms of performance and price are sold under the name of “graphene”. This leads to a mismatch in expectations and can to a disappointment/disillusionment due to high promises (“stronger than steel”) and first tests with wrong material. The risk is therefore high that the market gets damaged by companies selling carbon based material with 20+ layers as graphene without further clarification. It is important that graphene and 2D material suppliers get their products characterized from an independent institution. The variety and uncertainty of supply makes it complicated for application companies to decide which material to go for. This is already partially tackled by industrial self-regulation on national level, e.g. in Spain the National Association of producers and users of graphene with relevant producers such as Antolin, Avanzare and Graphenea and end users such as AIRBUS and REPSOL have adopted industrial standards for the characterization and labelling of graphene materials. This needs to be enhanced to EU or even worldwide level.

Besides this lack of clarity of the supplied materials, there is also more knowledge needed on the quality of material needed for a particular application. The material properties and its interaction with the host materials is still not comprehensively understood in a way that an application company can easily decide which graphene material to go for. Often it is still unclear which type of material (FLG, graphite flakes...) is best for the application (in terms of cost, quality and performance), e.g. in CFRP the sheets should not be too large in the filler. The needed amount and loading of material needed is also very relevant, especially as it determines cost-competitiveness. The goal should be to use the material that achieves the desired functionality for the lowest added cost, which is determined by quality of the graphene additive (higher quality will lead to higher cost), loading and process of integration.

Due to the lack of standardization there is also no quality assurance and quality control in place, which also hinders market uptake. Application companies need a second source for similar quality material, which is nowadays controllable, possible and not available. A steady, assured and controlled supply is today not yet available.

In order for graphene materials to be broadly applicable also **health and safety** issues have to be addressed based on industry standards (e.g. REACH not conducted yet). This is also depending on a prior standardization. In particular the health and safety aspect needs to be thoroughly addressed as the danger is high that graphene can be perceived as harmful by the broader public, although it might not actually be harmful in the applied form. This is particularly relevant when the material can be exposed due to wear (surface properties/lubrication) or combustion/decomposition.

As soon as a standardisation is available also the important topics such as end of life, environmental compatibility, acceptability from a regulatory point of view for different applications (e.g. in food, medical applications, drinking water) need to be addressed.

### **3.2.2.2 Cost/benefit often not yet clear**

Cost for nano-graphite, graphene nanoplatelets and few layer graphene and can range from \$20/kg to \$2000/g depending on quality and ordered amount. The cost for platelets with 11-100 layers ranges from \$20-\$1000/kgj with variable quality (lateral size, oxygen content, BET). The cost of production and of graphene materials is expected to decrease further with target prices for 2020 of €125/kg for high BET few layers and low oxygen content graphene and €25 to €35/kg for platelets with 11-30 layers,, as supplying companies are ramping up and scale to industrial quantities. For low quality graphene, actually an oversupply/overcapacity is claimed [165].

Undoubtedly, adding graphene or 2D materials to a composite will lead to added costs, depending on the loading and quality of used material. It is therefore of utmost importance to objectively clarify the cost/benefit towards competing technologies and the state of the art. The costs are to a certain extent controllable and foreseeable, however, also the actual benefits need to be made clear. This means that it is not enough to compare the composite with the unmodified base material, but there is also a fair comparison with state of the art or competing technologies needed. The goal needs to be to clearly show what added benefit graphene/2D additives can achieve in applications towards the currently used materials or whether it can achieve something that cannot be achieved otherwise.

Currently, improvements are not enough proven in relevant environments, i.e. often a real proof of principle is missing and tests are only under artificial circumstances. For a further feasibility study, it is important to show the potential in demonstrators relevant for

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j Consolidated values from Haydale, Future Markets Inc., Avanzare and Fullerex

the later application. That also includes testing a set of relevant parameters (e.g. tensile strength and fracture toughness), rather than testing for improvement of single parameters. With that, an objective evaluation of cost/benefit is possible.

There is a feedback from industry stating that lab developments do not go through to products, because not all scientifically interesting effects are commercial viable, although some are encouraging. A problem is the uncertain credibility of some published papers and measured improvements.

The cost and comparison to competing technologies issue becomes even more severe, when the host material is cheap, e.g. PP, PE or engineering polymers, where the polymer on its own costs 1-6€/kg. Adding a graphene material at a loading of 1-3% can easily double or triple the material cost only. It then would need to compete with performance polymers that are typically priced 3-20 times higher than engineering polymers (average 12\$/kg [166]). The comparison with other materials achieving similar properties is of highest importance for this case.

Graphene can often replace conductive carbon black in composites to improve conductivity. As lower loadings are needed to get similar or better effects, material is saved. If the loading is reduced by a factor of 10, graphene materials should not cost much more than 10 times the carbon black price (carbon black ~1-2€/kg for carbon black used as filler in the rubber industry, and for conductive carbon black ~16-60€/kg on ton scale). Recently Avanzare and Ashland have introduced in the market an electrically conductive composite based on epoxyvinylester resin (resin alone costs less than 1,5 €/kg)

A next necessity is to also meet the requirements for use in larger markets, e.g. automotive, aviation, packaging (thermal stability, durability, abrasion, qualification, cost). This also includes taking into account life and failure mode prediction and demonstrate lifecycle cost savings. Many commodity products, but also often higher priced products to not allow a higher price point, even when functionalities are improved. Therefore the lifecycle cost savings are essential for a cost/benefit assessment.

Several potential application companies expressed that the current performance improvements are not good enough for the price/effort. In particular for materials that are currently already cost prohibitive to be widely used (e.g. CFRP in automotive despite in high class cars). Prices for graphene materials are expected to go down, which can in turn improve the cost-benefit.

Last but not least, bulk graphene platelets are black in colour, which could have an effect on the applicability of composites due to colour constraints (where a colour coating is not desirable). This particularly applies to applications addressing thermal conductivity or electrical conductivity according to an industrial expert assessment based on market feedback.

The actual achievable tuneability of electromagnetic transmission needs to be communicated more clearly to possible stakeholders before this promise will be accepted in the industry. At the moment, numbers like 3% light absorption per layer of graphene are widely accepted as a universal truth.

### **3.2.2.2.3 (Potentially negative) Influence on processability of host material and component**

For the effectiveness of the additive and reproducibility it is crucial to have the adequate dispersion of the filler depending on the application. Larger platelets of 2D materials are dispersible with the right viscosity, functionalization or dispersing agent. This dispersion is a crucial step and needs to be well designed to reach the desired effects to overcome a lack of solubility/dispersibility (at high loading) and poor blending with host matrix. It is, however, also a process that adds another degree of freedom needing technical expertise and the formulation takes time for each application case. Furthermore, dispersion/functionalization processes need to be available at sufficient scale to not become a bottleneck.

Although graphene or other 2D materials are typically added at relatively low loadings, they can influence the processability of the host material (rheology, e.g. viscosity). This is for example seen in the workability of cement that is exacerbated when GO is added. [128], or in epoxy resins, and most of the thermoplastics when GO, rGO and few layer graphene are used as filler. Changes in the viscosity are also observed in polymers [167], although the changes are smaller than for CNT [168]. This can have positive or negative effects depending on the process (extrusion, molding, ...). The addition of a 2D material filler will most probably require at least a change of other processing parameters (sintering, extrusion, assembly). In the worst case, which appears to be the exception, different preparation techniques for components need to be applied (e.g. due to changed process). Additionally, the further processing of the components, such as joining, pressing, could be influenced. This needs to be investigated. The implementation barrier is lowest, where least changes are required. The goal should be to adapt the resin/polymer/host with graphene in a way that the manufacturing does not need to change tremendously, because changing a manufacturing process is very difficult nowadays.

For 3D printing materials graphene materials might be problematic for powder-bed sintering applications due to promotion of crystallization and in photopolymerization techniques due to reduced optical intrusion depth.

The need for safety precautions in production and the related effort for that are is also important and could become a weakness. First good practice protocols do minimize the release in production are available. However, most material production demands a certain degree of safety precautions, so that this is not a severe issue.

#### **3.2.2.2.4 Processing challenges in metals and ceramics and low maturity**

Processing GRM in metals or ceramics is more challenging than processing in polymers, due to the high temperatures needed for melting or sintering these materials. Issues such as carbide formation during high temperature processing need to be addressed.

The field of graphene-based metal or ceramic composites is much less mature than the one of polymer composites. However, proving that including GRM in these novel matrices leads to improved properties or cost/performance benefits while addressing the current weaknesses of these technologies (see 3.2.1.1.5), could spur industrial interest, given the large potential market size accessible for ultra-light metals or machinable ceramics.

#### **3.2.2.2.5 Current missing links in supply chain for graphene integration**

The value/supply chain of composite materials is currently not well covered in the graphene composites research and the graphene flagship. In particular in terms of prepreg integration and development, there are not many stakeholders involved. This opens up a missing link between material suppliers (e.g. resin and graphene producers) and final integrators (e.g. automotive or aerospace companies). It might be even needed that graphene materials will add another step in the value chain in form of companies doing predispersions mixing, before the materials go to compounders. This step could also be provided by graphene suppliers. Besides, graphene is not yet highly recognized in market driven composites communities.

### **3.2.3 KPIs for composites**

The following chapter summarizes important qualitative and quantitative technical and non-technical KPIs for composite materials.

#### **3.2.3.1 General KPIs**

##### **3.2.3.1.1 Recyclability and combustibility**

For many applications, recyclability, combustibility (residue free combustion in standard waste treatment) and biocompatibility/biodegradation when released to the environment are needed.

### 3.2.3.1.2 Cost

Table 11: Allowed added cost per kg saved (same table as Table 10).

Sector	Allowed added cost per kg saved (roughly)
Automotive	<3€ (mass market) -8€ (premium market)
Aviation	Few 100€ (depending on aircraft)
Space	Few 1000€ to 10000€

CFRP (automotive): average 100€/kg (material ~20-24€/kg), goal is 30€/kg (processing optimization) [169]

GFRP (automotive): 4.1\$/kg (material price) [166]

Flame retardant: average revenue per shipping unit: \$2.1/kg [162]

Impact modifier: 2.7\$/kg (average) [162]

Engineering polymers: 1-6€/kg

Performance polymers: average 12\$/kg [166], up to 100\$/kg

Carbon black: 1-2\$/kg as filler; conductive carbon blacks 16 €/to to 60 €/kg (on tonne scale)

### 3.2.3.2 Technical KPIs

For these KPIs it must be clear that just improving the properties of a given material is less relevant for industry; rather the improvement must be achieved at lower cost or other advantages relative to other, already existing materials.

#### 3.2.3.2.1 Mechanical

Youngs modulus: (elastic modulus): increase

Tensile strength: maximum stress that a material can withstand while being stretched or pulled before failing or breaking: increase

Fracture toughness: describes the ability of a material containing a crack to resist fracture, it is the critical value of the stress intensity factor (measured in MPa m<sup>1/2</sup>) Toughness: also toughness modulus: the area under the stress-strain curve and thus the dissipated energy per unit volume; this is much more structural-size dependent and thus less significant than fracture toughness

Look and feel, anti-squeak properties

Tribological properties: Friction, wear rate, (micro-) hardness (wear effects also important for health assessment)

Mechanics at elevated temperatures (and at extremely low temperatures)

Table 12 summarizes a few KPIs of typical composites on the market.

Table 12: Few examples of KPIs of composites for mechanical applications

Composite	CFRP PPS	CFRP TPU	GFRP PPS/TPU	CFRP Nylon	PAN Standart	Carbon Intermediate	Fiber High	Rods: CFRP-EP (unidir.)
<b>Recyclability and combustibility</b>	"Easily"	"Easily"		"Easily"				
<b>Density [g/cm<sup>3</sup>]</b>	1.58	1.5	1.8	1.58	~1.8	~1.8	~1.8	1.5
<b>Tensile modulus [GPa]</b>	117 (0° layup) 54 (0°/90° layup)	48 (0°/90° layup)	25 (0°/90° layup)	103 (0° layup)	230-255	275-310	310-600	130
<b>Tensile strength [MPa]</b>	1690 (0° layup) 780 (0°/90° layup)	710 (0°/90° layup)	430 (0°/90° layup)	1620 (0° layup)	3450-5000	4130-6370	1890-4900	1300
<b>Compressive Strength [MPa]</b>	930 (0° layup) 448 (0°/90° layup)			1000 (0° layup)				
<b>Company/Source</b>	Impactcomposites				Vectorply			Carbon-Werke

### 3.2.3.2.2 Electrical, thermal, barrier, flame retardant

Table 13: KPIs of components for electrical conductivity: [170]

$\Omega/\square$	Material	Description
$> 10^{13}$	Insulative	Insulators and Base Polymers. Not an ESD material
$10^9$ to $10^{12}$	Anti-Static	Initial charges are suppressed. Typically pink color.
$10^5$ to $10^9$	Dissipative	No or low initial charge. Prevents discharge to or from human contact
$10^3$ to $10^5$	Conductive	No initial charge. Provides path for charge to bleed-off. Typically black color.
$1$ to $10^3$	Shielding	EMI
$10^{-3}$ to $1$	Carbons	Carbon powders and fiber
$< 10^{-3}$	Metals	

Bipolar plates for PEMFC:  $>100$  S/cm (and  $>20$  W/mK thermal conductivity)

Bulk graphite in plane: 20-30000 S/m

Competition: metal coated carbon fibre, steel fibres

#### Thermal conductivity:

e.g.: Smart phone Graphite sheet (effective)  $d=25$   $\mu\text{m}$ ,  $k_{xy} = 400$  W/mK,  $k_z = 10$  W/mK, Heat capacity  $1.520\text{E}+06$  J/Km<sup>3</sup> [171]

Thermally enhanced commercially available polymers have thermal conductivities of 1-20 W/mK, sometimes 30 W/mK (PP or PA6) using organic fillers ( e.g. graphite), metallic fillers (e.g. copper) or ceramic fillers (e.g. boron nitride) at high loading (up to 80wt.%) [172].

**Barrier:** Permeability to gases/liquids/ions, water uptake in epoxies

**Flame retardant:** flammability, smoke and toxicity tests (FST)

Table 14 and Table 15 show some exemplary KPIs of marketed products.

Table 14: Some KPIs of thermally/electrically conductive or other composites.

Material/Composite	ECOPHIT	CFRC	PPS	LCP	TECACOM P@PA66	TECACOMP@PP S
<b>Type</b>	Graphite in plasterboard	High temp. applications	Therm. & electr. cond.	Therm. & electr cond.	Therm. Cond.	Therm & Electr. conf.
<b>Density [g/cm<sup>3</sup>]</b>		1.55	1.71	1.84	1.48	2
<b>Tensile modulus [GPa]</b>			17.5	24.3	8	15.1
<b>Tensile strength [MPa]</b>	2.5	400	70	80	55	
<b>Electrical conductivity</b>				1 [ $\Omega/\square$ ]	<104 [ $\Omega$ ]	1.42 x 10 <sup>4</sup> [S/m]
<b>Thermal conductivity [W/(m•K)] (in plane)</b>	0.52		6	20	11.2	85.8
<b>Thermal diffusivity [cm<sup>2</sup>/s]</b>			0.0322	0.1	0.051	0.1523
<b>Barrier properties</b>	99.99% absorption of em waves					
<b>Flame retardant</b>				V0 (@1,5mm) [UL 94]	HB [UL 94]	V0 [UL 94]
<b>Company/Source</b>	SGL Carbon		Coolpolymers		Ensinger	

Table 15: Some KPIs of thermally/electrically conductive or other composites

Material/Composite	TECACOMP®PA66 ID	TECACOMP®PEEK TRM	TECAPEEK450CF30	Ultrason®
Type	Detectable compound	Tribologically & mechanically optimised compounds	High temperature plastics	GFRP/CFRP with PPS, PES
Density [g/cm <sup>3</sup> ]		1.5	1.41	
Tensile modulus [GPa]		12.5	23	32
Tensile strength [MPa]		155	240	250
Compressive Strength [MPa]		180		
Tribological properties		"very good bearing and wear properties"		Wear and impact resistance
Thermal conductivity [W/(m•K)] (in plane)		0.9		
Barrier properties				Chemical, fuel, and oil resistant
Flame retardant			Melting: 343°C	Excellent FST behavior
Company/Source	Ensinger			BASF Aerospace

### 3.2.3.2.3 Processing

Compatibility with standard infusion, molding, prepreg, mixing, processes

Influence on viscosity, workability, temperature, curing of composite material during manufacturing

Compatibility with shaping, joining processes

## 3.2.4 Roadmap for composites

### 3.2.4.1 Current Maturity: First niche products are in the market

The maturity of graphene based products depends strongly on the application. Potential improvements are shown in the lab, such as increased young's modulus, improved conductivity and barrier. However, improvements are often shown only for singular parameters. These lab results are often not yet transferred to relevant environments/scales. Additionally, the overall set of parameters is not improved good enough in some cases: For example in some cases although the mechanical strength of a composite increases, the elongation and energy absorption until breaking worsens, which is not good for impact performance. It remains to be investigated which 2D material combination/configuration, loading and host work best together for a targeted applications and how they compare to competing materials in terms of cost-performance.

Only in niche applications (fishing rods, sports equipment) first products advertise the use of graphene. These are areas, where new technologies can be used for advertisement.

In terms of carbon based conductors the maturity is still very low (much lower than for CNT).

#### **Products on the market or close to market:**

There are already products commercially available in the sports and leisure sector that advertise their graphene content. As the name graphene is not protected, it is often not clear whether the equipment actually contains graphene materials or rather graphite flakes or carbon black.

Table 16: First available products or products expected to hit the market soon that claim to use graphene in composite materials (as of March 2016).

Company	Product
Head	Tennis racket[173], skis
Vittoria	Bike tires
G-Rods	Fishing rods
Catlike	Cycle helmets
Colmar	Sport clothes
Sher-Wood Hockey	Hockey stick
Graphene 3D Labs	Conductive composite filaments for 3D printing
Angstrom Materials	Thermal Foil ( $k_{xy}=1500-1700\text{W/mK}$ , $d=25\mu\text{m}$ ), $>12000\text{ S/cm}$
Ashland Derakane	resin filled with graphene for conductivity

Other product ideas (not exhaustive): Condoms (2 years from now), rubber band with sensing capability, loud speaker cones based on PP+graphene (premium)

### 3.2.4.2 Barriers/challenges (summarized)

The following challenges summarize the most important issues that are also derived from the chapters on strengths and weaknesses as well as market opportunities and threats.

General challenges:

- Production of right quality (high or low) and functionalization are bottle necks
- Current graphene supply and uncertainty of quality (due to missing material standards), some self-regulatory are in implementation in Spain by graphene producers and some end-users as a first approach to solve it
- Transfer graphene properties to bulk material
- For the integrator or user, it is often unclear which material is best suited for the given purpose (quality, amount, functionalization)
- Show objective and real benefits in relevant environments looking at
- Cost/benefit: crucial, and to a large extent not yet clear or based on “assumptions”, especially important for cost sensitive markets (automotive, consumer).
- System and life cycle cost assessment
- Unclear end of life properties (combustion, recycling, biodegradation)
- Life cycle health and safety (working place, release in operation, end of life)

**Process related challenges:**

- Lack of technical expertise for applications
- Finding the right formulation takes time
- Reproducibility of large scale homogenization, dispersion and mixing in the respective solvent or matrix throughout the processes (from base material to final part/matrix) to reach and maintain an even distribution, e.g. for CFRP during infusion or prepreg. This was a “killer” for CNT/pellets/buckyballs
- In-situ methods to produce graphene (exfoliation in a thermosetting polymer or other matrix)
- For real electrical conductors, a process needs to be found (yarns?)

**Value/supply chain and eco-system:**

- Insufficient readily accessible data and design tools (standardized material property database) using performance standards
- The lack of standardization leads to the problem that all these very different materials in terms of performance and price are sold under the name of “graphene”. Due to the lack of standardization there is also no quality assurance and quality control in place, which also hinders market uptake. Standardization as a bottle neck: after that QA/QC, REACH etc can be approached
- Supply/value chain not yet developed, might need to be adapted
- Established and conservative supply chains
- Flagship: value chain not enough covered, e.g. component supplier for automotive missing. End-users/OEMs only do testing, but integration and innovation is done at component or prepreg/masterbatch supplier level (tier 1 and 2).

**Thermal and electrical conductive composites:**

- Anisotropy: If controllable, the anisotropy of transport can be strength, but until that this induces and additional barrier, as it is more complicated than an isotropic material.
- For higher currents: bulk transport needed, which needs a 3D architecture to increase the overall transported power and current
- Black colour often not desirable

**3.2.4.3 Potential actions**

If the area of graphene/2D in composites is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

**Basic understanding:**

- Graphene/matrix interaction deserves further studying (to transfer the properties of graphene to the matrix)
- Study and understand functionalization
- more knowledge needed on the quality of material needed for a particular application (systematic investigation of material) and education for end users to clarify the open question which material needs to be used (1-2 layer, few layer, nano-graphite...) and to manage expectations; this can be supported by predictive modelling
- Study dispersion/aggregation in matrix systems
- How to control isotropy/anisotropy with simple processes (for conductivity)
- Clear proof and an open discussion on Health & Safety is needed

- Is there any intrinsic biodegradability of graphene? Or would graphene rather come out unchanged from biodegradation of the surrounding matrix?
- Investigate actual achievable tuneability of electromagnetic transmission. At the moment, numbers like 3% light absorption per layer of graphene are widely accepted as a universal truth.

Many other actions are related to engineering problems and extensive testing.

Product development:

- “Flashes of positivity”/lab scale developments now need to be further elaborated and transferred to real environments to allow further uptake from industry
- Look at relevant sets of parameters needed for a particular application
- Make use of established standards, characterisation methods and norms for semi finished products, applications and materials where graphene is integrated
- Compare results to competing materials or technologies addressing the same functionality
  - o This is particularly relevant for enhancement of host materials, which need to be compared to other materials that achieve a similar property (and not just to the plain host material)
- Address system and life cycle costs instead of only added cost through a new material

Processes:

- Scale up of production of 2D materials with needed quality (be it low or high)
- Develop large scale and mass production compatible functionalization methods
- Understand influence of 2D additives on processing of matrix materials, also in terms of post processing of parts, such as gluing, soldering...
- Investigate 3D printing
- Investigate the potentials for in-situ exfoliation

Testing:

- Durability tests needed (accelerated testing...) to know long term performance
- Test of effective packing and transit and shelf life of intermediates
- Show biodegradability/recyclability or residue free combustion in hosts (is graphene found in exhausts of waste combustion or is it decomposed?)
- Show compatibility with environment (for use in drinking water) to add it to the positive list of allowed materials and make it acceptable from a regulatory point of view
- Study the release of graphene from the host under crash, breaking, heat and other circumstances
- For flame retardant: “FST” Fire smoke toxicity, especially “ST” need to be tested according to targeted applications (cars, planes, trains, underground...)

Value/supply chain and eco-system:

- Enhance interaction with prepreg/compounder and component manufacturers to close the gap between researcher, graphene supplier and final user
- Manage expectations objectively
- Establish material standards and databases
- Bring national initiatives on self-regulation to EU or worldwide level
- Establish standardized methods to determine the quality of produced graphene and other 2D materials (“certification”)

- Create a group of classification criteria in order to evaluate the produced materials to help manufacturers and customers to
  - o classify their material quality and customers
  - o provide an expectation of the performance of the classified graphene and
  - o decide whether or not the graphene or other 2D material quality is potentially suitable for various applications

#### 3.2.4.4 Roadmap

**Mechanical, electrical & thermal enhanced composites:** broader niche markets will be addressed in the near future. More markets will be addressable in the next 3-5 years and the evolution of the market will be in parallel of the scale up of the graphene materials. Mass markets are expected not before 10 years.

**Barrier properties:** Marketable solutions are expected within 5-10 years.

**Flame retardant:** Broader marketable solutions are expected before 5 years, some very positive results has been achieved in thermosets, thermoplastics and even in textile industry. Rather addressed “alongside” with other functionalities as for flame retardancy only many solutions are available.

**Further time related aspects depending on addressed sector:**

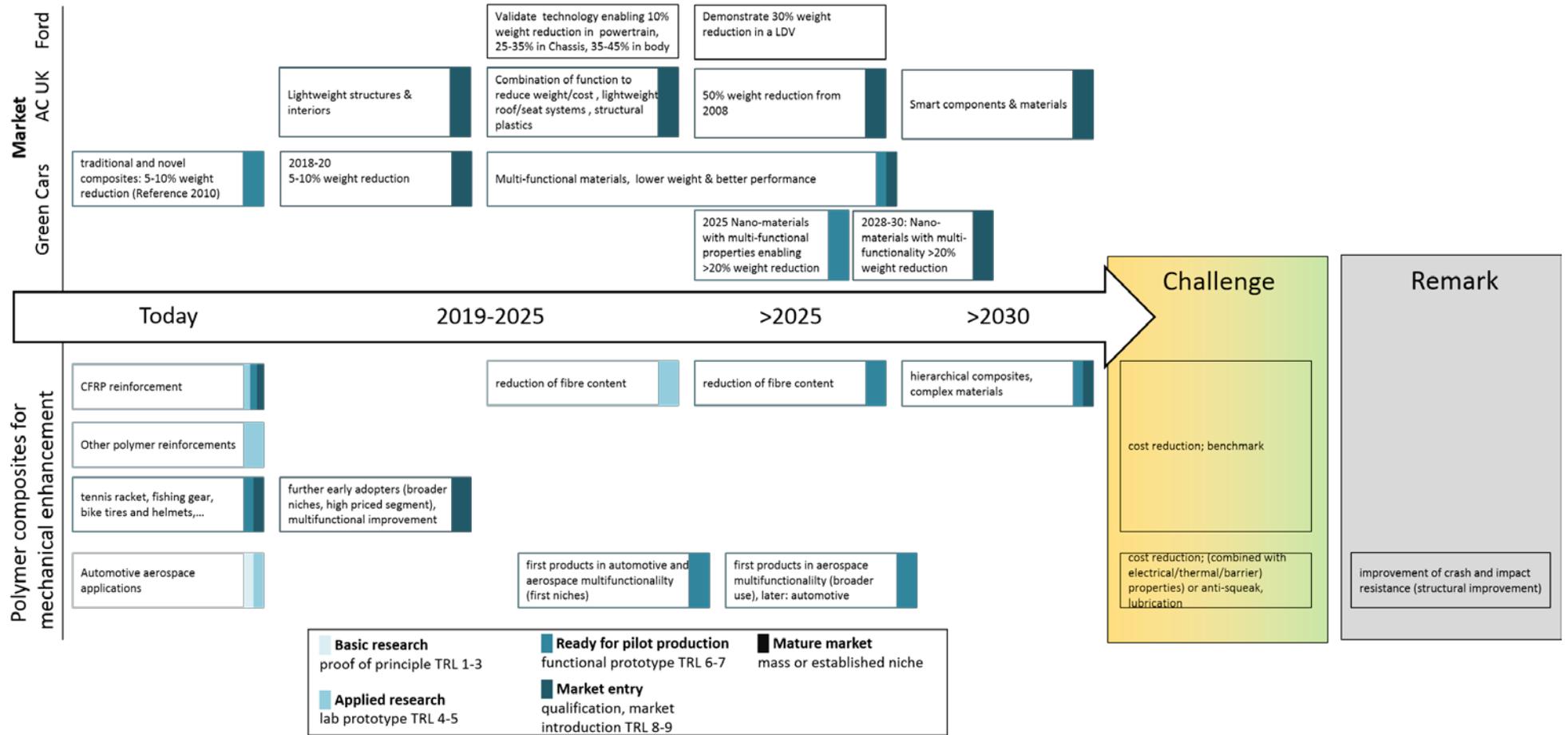
##### **Automotive:**

Lead time after “first testing”: 4 years until market intro in automotive

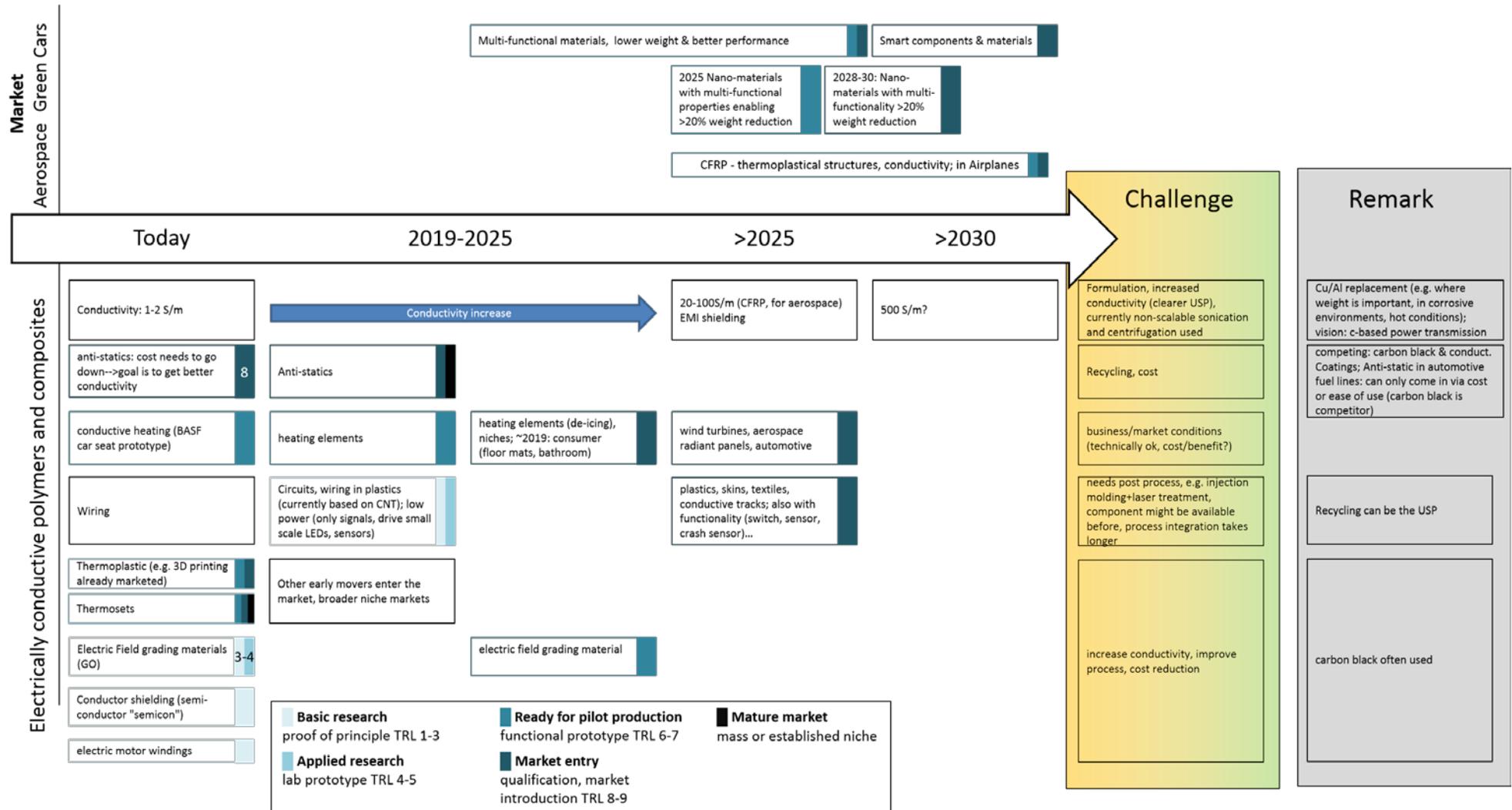
High price point: currently only high value cars (niche)

##### **Aerospace:**

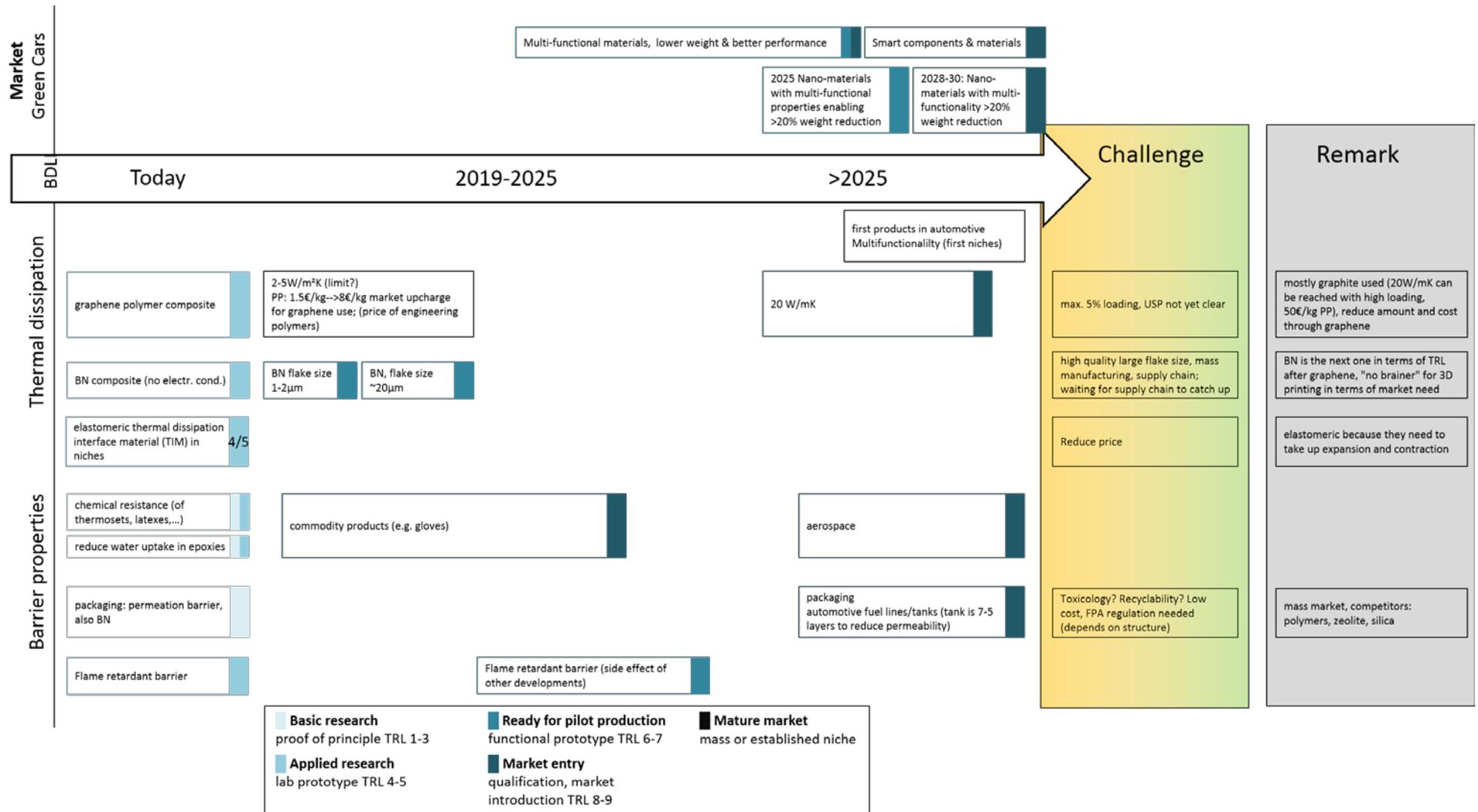
It typically takes 10 to 15 years for a new air frame technology from basic principals until operational maturity (speed up is addressed currently).



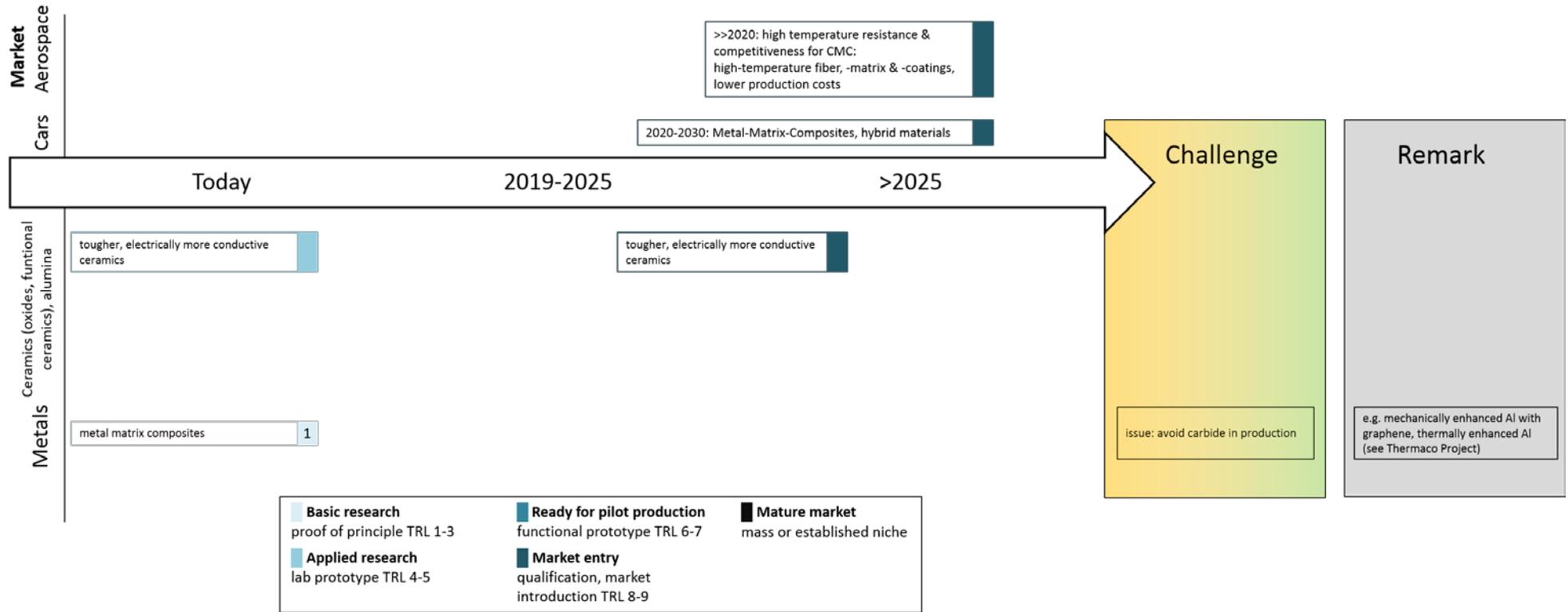
Sources: Ford [174], AC UK [175], Green Cars [176, 177]



Sources: Green Cars [176, 177], BDLI [178]



Sources: Green Cars [176, 177]



Sources: AC UK [175], BDLI [178]

### **Electric field grading material for high voltage insulation**

Composites have many different potential applications, sometimes with very special properties and requirements. This box introduces one special applications, i.e. the use as electric field grading material.

The field dependent conductivity (or rather isolation) helps to avoid discharge in isolators for high voltage applications (e.g. in HVDC cable joints), because field peaks and to large field gradients leading to discharge are avoided in the isolation of a cable. This is needed because ever higher voltages and lighter cables are used in power transmission.

GO can be used in a polymer matrix (e.g. 3% in Si-rubber) as a field grading material. It increases the resistance and renders it more field dependent, i.e. having a lower resistance at higher fields. Through that, voltage peaks are avoided. The best case would be a switching behaviour at a certain field threshold. It has been observed that the conductivity switches by 6 orders of magnitude (from  $10^{14}$  to  $10^{11}$   $\Omega/m$ ). [179]

The composite competes with SiC or ZnO particles and carbon black in a polymer matrix. Its benefits are that it is stronger and more flexible. Furthermore, it is possible to control and design the electrical properties to a certain extent and allows going to higher fields and thus higher voltage levels. Current issues are the long-term stability. Further understanding and testing, especially of reliability and performance are needed. Another barrier is the conservativeness of customers, e.g. Si-rubber is still a new material and is around since the 90ies. The horizon for commercialisation is on the order of 10 years.

In 2014 4.5b€ revenue was created in Europe with insulated electrical conductors for voltages above 1000V. [155]

### **3.2.5 Conclusion for composites**

The variety of potential applications with early adopters makes composites a very interesting application area. Additionally, the graphene material can be prepared rather simply and cheap and graphene platelets are often sufficient. These platelets are becoming cheaper and with that the barrier for broader use is reduced. Functionalization plays an important role for this area, as the particles have to be well dispersed in the host material to gain the largest effects.

The USP for graphene use in this area is the multifunctionality, because it can increase mechanical strength, electrical and thermal conductivity, barrier properties, surface properties (lubrication) and flame retardancy at the same time.

Although the actual cost-benefit of is not yet known for most applications, the maturity compared to other potential application areas of graphene/2D materials is already quite high and first products are on the market. The sheer number of possible applications on the other hand makes it hard for researchers to address particular products.

Most important for a further market introduction is standardization and testing for health and safety and recycling/end-of-life properties. Besides, the demand oriented communities need to be made aware of the actual benefits and expectations need to be managed. The risk is still high that the expectations are too high (100x stronger than steel), which cannot be reached. Additionally, the perception of “graphene is the next CNT” reduces the interest from many conservative stakeholders.

Table 17: Assessment of market and technological potential of graphene/2D materials use in composites on a scale - -, -, 0, +, ++.

<b>Composite property/host</b>	<b>Current technological potential (USP)</b>	<b>Market potential (EU perspective)</b>
<b>Mechanical enhancement</b>	+	++
<b>Thermal enhancement (polymers, ceramics)</b>	+	++
<b>Electrical enhancement (polymers, ceramics)</b>	+	++
<b>Barrier (polymers)</b>	+	++
<b>Flame retardant (polymers)</b>	0	+
<b>Multifunctional enhancement, added functionalities</b>	++	++
<b>Metals</b>	0	+
<b>Polymers</b>	+	++
<b>Ceramics</b>	+	++
<b>Cement/concrete</b>	0	+

### 3.3 FOCUS: Anti-corrosion coatings

This chapter deals with graphene coatings or enhanced coatings and paints. Large scale (square meter) coatings/varnishes/paints for industrial applications are addressed, with a particular focus on anti-corrosion applications.

From a technological point of view, coatings can be prepared from bulk graphene/2D platelets (usually used as paints or inks) or from pristine graphene or few layer graphene (usually prepared by chemical vapor deposition and then transferred onto the host). For coatings and inks, 2D materials can be used as additives similar to composites to enhance properties of common coatings. In principle 2D materials are a perfect candidate for coatings due to their sheet character and large lateral size.

#### 3.3.1 General context: Coatings

Anti-corrosion coatings are applied particularly to metal and fibre composite substrates that are subjected to harsh conditions (e.g. in electrolytic liquid phase or gas phase under elevated temperatures). Organic coating solutions are often applied in building and construction, food packaging, automotive and marine. They consist of a complex system of binders, pigments, fillers, additives and solvents. The coating solution must provide both good adhesion to the substrate as well as different functionalities which range from protection of the substrate, to self-stability, e.g. chemical / mechanical / UV stability, which influence its longevity. Pigments may be used to improve the corrosion protection properties of coatings. Incorporation of flake-shaped particles parallel to the substrate surface can effectively hinder the permeation of corrosive species into the coating and to the substrate surface. Other approaches make use of sacrificial pigments with an electrochemical preference for corrosion over the protected substrate material. Often, coatings consist of multiple layers, with each of them fulfilling different tasks in the coating system. The specific amount and type of layers varies significantly depending on the application scenario, and can even vary in the same application. Aside from the desired performance, coatings and coating systems must comply with common cost constraints.

##### 3.3.1.1 Market situation for anti-corrosion coatings

Corrosion accounts for huge financial losses in major industries. The overall market for coatings and paints is estimated to be >100 billion € in 2014 with a growth rate of CAGR ~5 % until 2020 where it reaches a projected 130 billion [180] €. In comparison, the world market for anti-corrosion coatings is estimated at 22 billion € yearly, with largest shares in Asia followed by the US and Europe. Largest markets for anti-corrosion coatings include construction, aerospace, automotive, oil and gas, and marine industries. Among classical applications for ships, which are subject to harsh environmental factors like salt-water and pressure, steel for bridges and buildings, new applications like off-shore installations for power generation and resource development are driving the coatings market.

There is a significant industrial base in Europe for coatings, varnishes and paints. Relevant production value was on the order of €19 billion in 2014, with a CAGR of 2.3 % from 2012 to 2014 [155]. Figure 2 also shows that the innovation and patent capacity is high in Europe in terms of transnational patents. European industry is in one league with USA and Japan.

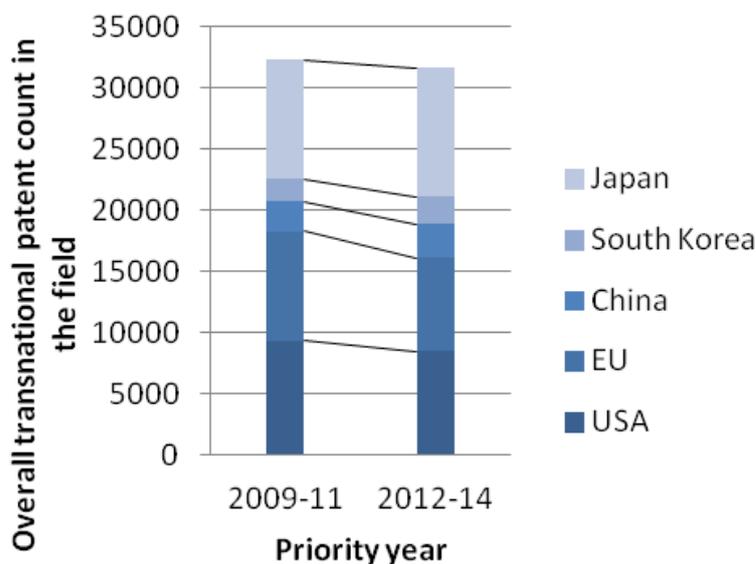


Figure 38: Overall transnational patent count in surfaces and coatings. 2012-2014 values are projected. [137]

### 3.3.1.2 Market framework conditions

Coating formulation manufacturing constitutes an established market with a large range of diversified suppliers. Many alternative concepts already exist, some of them with proven records of lasting up to 30 years in application. That being said, legislation and global competitors will pose the main drivers for **new developments** in the corrosion protection market. Due to current and expected regulations on European and (inter-) national level<sup>11</sup>, more eco-friendly production and components of anti-corrosion coatings and paint systems experience an upward trend. Consequently, waterborne, ultraviolet cure (UV) and powder coatings are increasingly preferred over solvent borne coatings and paints [181]; and formerly common anti-corrosive coating contents, such as chromium trioxide, need to be substituted.

<sup>11</sup> Being such as the European REACH programme for improving the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances, and the European VOC Solvents Emissions Directive.

### 3.3.1.3 Perspectives for graphene

Graphene is discussed as additive or pigment in coatings for several of its properties. The hydrophobicity [182] of the material can be utilized to achieve self-cleaning, antibacterial and anti-biofouling [183] properties on the substrate surface. Its chemical inertness and high aspect ratio can lead to the build-up of excellent barrier layers if sufficient orientation and density of the particles is achieved during the coating process. It has been shown that GO can effectively decrease the oxygen permeability of PEI, form a water vapour barrier or act as an anti-corrosion coating if directly applied on metal substrates [184]. Promising results with electrochemically generated graphene, that is even easier to produce than GO, showed a reduction of oxygen transfer rate of up to 90 % [185]. Other scientific publications consider the ability of graphene enhancement to effectively suppress cathode delamination of the coating layer [186].

Accordingly, the number of patents in graphene surface & coatings technology shows that the USA is in the lead position and Europe on the second place (see Figure 1). Compared to the reference years 2009 – 2011, the number of patents with priority between 2012 – 2014 has nearly doubled, showing the significance of the topic and a certain progress from research to technology exploitation in this field.

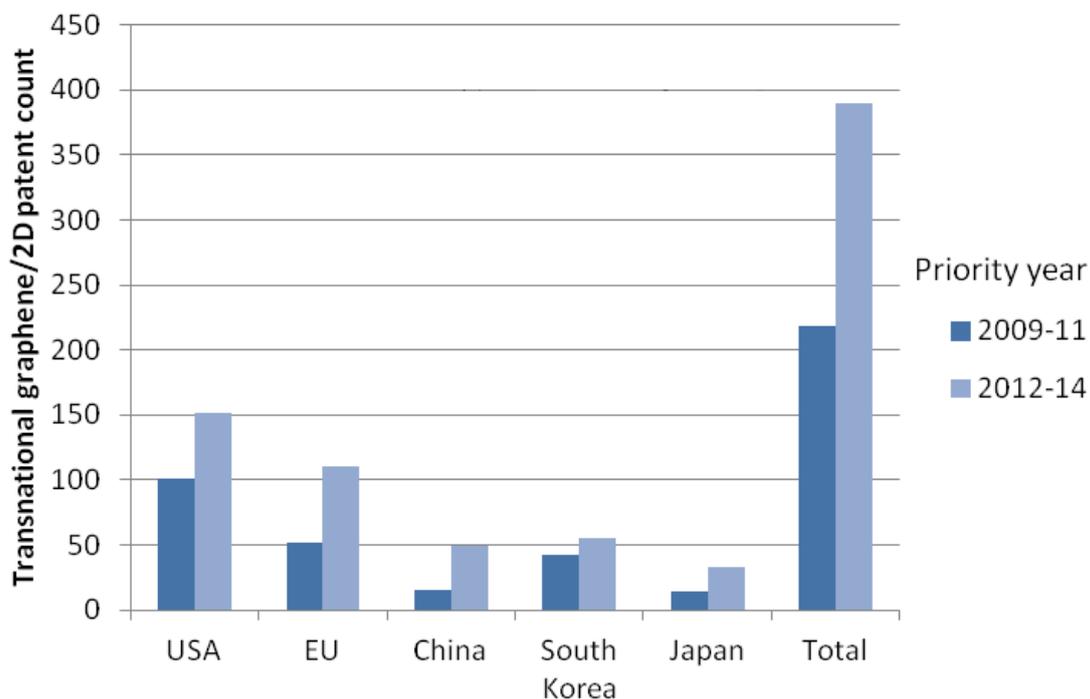


Figure 39: Patent analysis of graphene/2D materials in surfaces and coatings: Number of graphene related transnational patents in 2009-2011 and 2012-2014. 2012-2014 values are projected. [137]

### **3.3.2 Corrosion mitigation in aerospace, automotive, and marine contexts**

Traditional European industries facing global competition and high sensitivity to more restrictive environmental legislation. The selected application cases differ significantly in terms of the susceptible substrate material, corrosive environmental factors, allowable budget, and targeted duration of protection and maintenance cycles. They represent traditional European industries active on truly globalized markets with intense competition. In each case, their core business is centred on complex equipment being operated under uncontrolled environmental conditions.

#### **3.3.2.1 Anti-corrosion in the aerospace industry**

Corrosion protection is an important subject within the aerospace industry with specific regard to interior structures that may be in contact with moisture or highly corrosive substances such as hydraulic fluids. Highest safety demands and regulations demand absolute corrosion control throughout the plane lifetime of about 30 years. Intense qualification processes and efforts translate to a conservative industry with rather high entrance barriers for novel products, particularly as accelerated testing techniques cannot offer reliable support and new products require long-term testing in the genuine application. Nevertheless, as customers desire high reliability with no or little need for regular maintenances, reduction of necessary efforts may provide a unique selling proposition for novel products. Subjects of consideration include the protection of fuel tanks, of major supporting elements providing structural integrity, and contact to hydraulic fluids as most corrosive chemical inherently present in airplanes.

Coating substrates relevant in this context are fibre composites used as structural elements or tank linings on underlying metal structures, aluminium alloys containing zinc and copper, and stainless steel. In helicopters, titan and steel are used for connecting elements and magnesium is investigated as structural element. As large surfaces are characteristic for airplane components, immersion application and spray coating are preferred for achieving corrosion protection.

#### **3.3.2.2 Anti-corrosion in the automotive industry**

Passenger cars constitute the archetypal high value mass product primarily sold to consumers as customers. Regular corrosion maintenance appears rather uncommon in the market, so that any initial anti-corrosion treatment has to endure the whole typical product lifetime. Exterior, interior, and power train categorize the major application areas for coatings, where environmental conditions, common wear and tear, and operational specifics constitute the main durability concerns, respectively. Various steel types constitute the classical material class in the industry, but other metals and fibre composites find widespread and increasing application.

Commonly used anti-corrosive coating types for passenger cars bodies are electro-deposited coatings as well as diverse paint systems. Initial galvanic coatings usually provide a sacrificial anode material such as zinc. On top of the coatings, different paint systems are applied to the car components, depending on their respective corrosion requirements. Such paint systems usually consist of a base coat and several further coats of different functions, which can be solvent borne, waterborne, powder and UV coatings.

### **3.3.2.3 Anti-corrosion for marine applications**

Fright ship lines operate a multitude of large vessels in constant (below waterline) or coincidental (structures on deck) contact with the challenging marine environment promoting both corrosion and fouling. The formation and expansion of biological films on the hull (fouling) severely increases friction and fuel consumption, but also promotes corrosion. Heavy-duty coatings need to control both effects, with serious impacts on the economics of operation (maintenance cycles, fuel consumption). In particular, micro-level roughness promotes the adhesion of initial organic growth.

Environmental protection and related regulatory efforts necessitate novel solutions beyond traditional chromate and biocide based products with severe impacts. Typical coating systems rely on very thick layers with slow intended wear and regular replacement (on cycles of 60 or even 30 months). An alternative technology based on durable silicone coatings promised superior durability, but failed in terms of producing much higher than expected biological fouling. The industry desires novel high-volume but low-cost products, might be rather open to innovation, including the provision of large-scale test areas for realistic in operation testing.

Depending on the depth of water, offshore wind turbines require different types of bases for stability, which range from mono- and multi-piles to floating bases and consist mainly of steel. As these components are in constant contact with water, their corrosion protection is of active and passive nature. This involves, amongst others, reactive and anti-microbial coatings. Steel junctions connect the hollow steel tower to the base, which in turn supports the wind turbine and the connected blades. Main market opportunities for anti-corrosive coating and paint solutions lie within reducing maintenance hours of wind turbines, improving protection of mechanically stressed wind turbine parts, as well as improving paint technologies for areas inside the tower that are difficult to access.<sup>12</sup>

### **3.3.2.4 Market situation**

Applications of corrosion protection coatings and paint systems are manifold and diverse. As stated above, automotive, marine, and aerospace are amongst the largest addressable anti-corrosive coating market segments. The global automotive coatings and paints market was valued at 14 billion \$ in 2014 and is expected to grow with a CAGR of 5.5 % to ~19

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<sup>12</sup> See chapter 3.2.1. for elaboration.

billion \$ in 2020 [181]. Other sources estimate 5.1 % CAGR and 11.3 billion \$, respectively. Passenger cars represent by far the largest market segment that is expected to drive the global automotive coatings market [187].

The global marine coatings market had a size of 7.7 billion \$ in 2013 with a growth of CAGR 6.5 % to rise to ~12 billion \$ by 2020. The shipping industry holds the largest share of the marine anti-corrosion coatings market, in particular for ship and vessel coatings [188, 189]. The progressing transformation of European and Asian energy systems towards renewable energy generation, offshore installations for power generation and their maintenance pose another relevant marine coatings market [190]. With 150 GW wind power capacity as compared to 170 GW installed in China and 159 GW in the USA, Europe is among the leading global wind energy producers [190]. In Europe, the North Sea is the main region for offshore deployment [191]. The global aerospace coatings market size, in terms of value, was estimated at 1.4 billion \$ in 2017 and is projected to grow at a CAGR of ~6 % to reach 1.9 billion \$ by 2022 [192].

### 3.3.2.5 European framework conditions

Corrosion management plays a considerable role in the European automotive, aerospace, and marine industries. Major enterprises often employ dedicated corrosion experts and maintain in-house quality control facilities for testing anti-corrosion measures. Thus, these industries possess longstanding experience and in-depth knowledge of mechanics and performance of various anti-corrosion solutions. Innovation opportunities in corrosion protection applications depend chiefly on legal developments and global competition.

Recent changes in European legislation require both new coating technologies, e.g. substitute technologies for hard chromium plating, and new materials or solution components. Thinking ahead, future legislation on European and national level might make it necessary to find replacements for common active anti-corrosion components, e.g. for zinc and nickel. Global competition and markets pose another relevant driver for the European coating market development. This is particularly apparent in the automotive and aerospace sector, while the marine energy production sector is still profiting from Europe's unique geographical features with its large inland water areas.<sup>13</sup> For maintaining its strong position in the offshore wind park market, Europe will need to increase the distance of offshore wind parks to land. Considering the therewith related more difficult maintenance conditions, developing anti-corrosive measures requiring even less maintenance hours than current solutions will be of interest to the industry. [34]

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<sup>13</sup> Other water areas are not suitable for offshore instalments due to harsher environmental conditions.

### **3.3.3 Direct innovation interface: Graphene for advanced anti-corrosion coatings**

At present, anti-corrosion function and underlying mechanism(s) of graphene remain under discussion – still hampering intensified commercialization efforts in the coating industry.

#### **3.3.3.1 Technological strengths and weaknesses for the use of graphene in advanced coatings**

2D materials are perfect candidates for coatings, as they have the thickness of one atomic layer, are flexible, stretchable and have large lateral dimensions to cover surfaces. Nonetheless, 2D materials can be applied as single or few layer large sheets or as flakes/platelets in paints or inks usually incorporated into a binder. The former usually achieves better functionalities, but the application of the coating is tricky, costly and not yet mass production compatible. The latter is much easier to apply and reaches also interesting properties, although high transparency is not possible yet.

In general, graphene and related materials are desired for their promise to provide multi-functional properties in (organic) coatings. In particular, the high mechanical stability of graphene can increase wear resistance of the surface film, while better thermal and/or electrical conductivity might be relevant for niche applications. While the intrinsic properties of graphene promise high potentials, basic technological aspects such as sufficient graphene dispersion or possible interface interactions in polymers still need to be explored. In the light of the complexity and diversity of modern coating systems, the application case of graphene might not be an entire alternative coating technology, but improving specific functions and replacing conventional layers in a coating stack. The application interest for graphene in the coating industry could strive as soon as replacing several layers and their function by a single (or at least fewer) layers(s) appears achievable. The overall reduction of the layer count by elimination of functional layers would not only reduce the overall material consumption, but also decrease the effort and time consumption of coating application – and constitute a unique selling proposition for many conceivable end customer.

Graphene coatings have also interesting electromagnetic properties, e.g. transparency or tuned absorption in certain wavelengths ranges. With the possibility to create multi-layer structures of different 2D materials, the versatility becomes even higher. Electroactive coatings, e.g. for electrochromic applications are potential areas of interest, where 2D inks could provide an interesting solution. Also tunable surfaces are possible, e.g. electrically conductive and transparent coatings with tunable wettability. [193]

##### **3.3.3.1.1 Controversial discussion about mechanisms and role of graphene**

However, a core bottleneck for anti-corrosion by graphene is its highly deputed functionality in this regard. Published claims range from highly promising [194] to literally 'worse than nothing' [195]. The incoherent literature situation directly relates to the challenge of graphene supply, where various types, such as GO, pure and functionalised graphene, are sold

with poor specification (particle size, thickness, purity, distribution, etc.) and lowest consistencies (even batch to batch). In combination with various application concepts, substrate materials, and testing conditions supposedly contradictory corrosion protection characteristics of graphene appear less surprising. In summary, several well-documented and scientifically sound publications reporting on promising anti-corrosion properties of graphene exist, but an established consensus on the nature of the underlying mechanism(s) has not been achieved yet. The most prominent claim of highly beneficial barrier properties (oxygen, water) appear substantial and rather undisputed.

Although graphene can be a good barrier for anti-corrosion, it also has some intrinsic drawbacks. Graphite is a very noble material and can lead to galvanic corrosion, so graphite residues can lead to detrimental effects [196]. Therefore, the graphene material used in an anti corrosion coating needs to be well defined and must not have too many layer in order to not promote corrosion, when in direct contact to the metal. Besides, it has been shown that on long term, graphene can enhance corrosion when in direct contact with the metal surface, probably due to its conductivity. [195] However, this may only occur if the surface to be protected is electrically conducted to the graphene species and not insulated by an organic coating as it is typically the case for varnishes, inks, etc. Such a multi-layer coating could be feasible, where graphene materials is one of the intermediate layers.

### **3.3.3.1.2 Unproven wear resistance, durability and lifetime of coatings**

Resistivity against wear and scratching are crucial for essentially all coatings. For graphene based coatings in order to be commercially viable, this mechanical stability under stress and over time needs to be proven. This also has to take into account the environment, where the material is supposed to be used (e.g. humidity, aggressive fluids, biologically active environments...). This property is probably mostly defined by the binder in inks/paints/pastes, but also different substrates need to be taken into account and the interaction of the coating with the substrate to avoid delamination. For coated fabrics, the washability and wear resistance is also important.

The commercialisation of anti-corrosion by graphene and even the allocation of substantial corporate research and development efforts in that direct critically depends on convincing scientific resolutions of the questions above. First of all, the nature of the anti-corrosion mechanisms largely determines if, in what extent, and where graphene may eventually be applied. For instance, when mainly relying on the barrier properties, a graphene-based coating system must certainly consist of graphene-free initial layers avoiding direct metal-carbon contact and, perhaps, well-designed sacrificial corrosion functions. Urgent challenges described by experts included possible mechanical indentation (How to avoid tiny coating flaws to turn into massive corrosion hot spots?) and sufficient graphene properties (How to avoid limitation of barrier function to the boundaries of individual graphene particles?). Convincing test result may not suffice for the paint industry as they may require detailed mechanistic concepts for being able to see to their own clients (see below).

In the light of legislation possibly driving anti-corrosion innovations by simply requiring replacement of established solutions with questionable environmental impact, the full resolution of toxicity concerns associated to graphene (and any other type of nano-scale material) could promote its consideration in the downstream innovation spheres.

### **3.3.3.2 Market opportunities and threats for the use of graphene in advanced coatings**

With the coatings and paint market being established and relevant to many applications, coating and paint innovations will have to compete with numerous and well-researched formulations. Current solutions in automotive, aerospace, and offshore production already provide cost-efficient and sufficient long-term protection. Graphene-enhanced coatings or paints consequently should provide more than corrosion protection, higher performance at same cost, or address niche markets.

Obvious bottleneck in this respect is the lack of data on graphene-enhanced or -based coatings. As mentioned above, neither experienced coating providers nor knowledgeable end-users will accept a new component or formulation without in-depth understanding of its mechanics and behavior in application.

Another threat, in particular for nano-coatings is the perception of environment, health and safety issues, in particular when the surfaces break and the coating is removed/exposed. Although the amount of material released might be low, it still needs to be addressed to avoid bad reputation and wrong perception.

Also in terms of regulatory requirements (exposure, peel off, wear, e.g. when used for lubrication), usually the requirements are rather high and strict. In particular for applications where contact is inevitable and intended health and safety have to be addressed. For biomedical applications, good manufacturing practice (GMP) is inevitable. Also anti-fouling or anti-microbial applications are very sensitive to health and safety and industry might be reluctant to consider nanomaterials (or the barrier will be high).

Facilitating collaborations between graphene research, coating providers, and end-user industry could help establishing data both for graphene producers and industry. A joint development could also facilitate engineering the Graphene component and application according to the specific requirements of the selected use case. Another advantage of such a setting would be the possibility to make use of the vast existing experience and expertise of the coatings industry and their end-users. Being that end-users prefer several providers for coating formulations of similar performance, setting up several joint developments appears recommendable.

When introducing a new material or formulation into the coatings industry, its processing costs, supply chain integration, and performance are most relevant criteria. Additionally, its introduction will depend on addressed end-user markets and therewith related production scale. Custom formulations for niche or luxury markets are less cost-restrictive as compared

to mass applications and therefore pose an opportunity for market entry of graphene-enhanced coatings or paints.

### **3.3.4 Indirect innovation interface: Corrosion control in aerospace, automotive, and marine context**

Legislation provides a window of opportunity to introduce innovative corrosion protection schemes – when compatible with challenging end customer demands.

#### **3.3.4.1 Technological strengths and weaknesses for the use of advanced coatings for aerospace, automotive and marine**

Beyond prevention of common electrochemical corrosion processes, the target applications fundamentally shape the coating demands in the various industries addressed. Aspects range from the variety of specific corrosion threats and closely related challenges specified by the application scenario to highly specific demands of multifunctionality tailored certain niche challenges. Only in the latter case, there might be opportunity to push innovative solutions by a unique selling proposition into these niche market as established solution might perform insufficiently, require extensive cost and/or application effort, or even simply do not exist quite yet. Some examples gathered in private expert consultations and workshop discussion include: (a) advanced mechanical wear and tear resistance (e.g. automotive door lock mechanics, wind turbine maintenance paths), (b) enhanced chemical tolerance (e.g. hydraulic fluids in air planes), (c) aesthetic aspects (e.g. automotive rim/break colours), or (d) biofilm growth control (e.g. freight ship hulls).

In general, all considered industries appear rather content with the established and readily available anti-corrosion solutions. Diffusion barriers for general coating innovation in the field appear very high and would require significant direct (coating supplies) or indirect (easier application, advanced longevity) cost advantages to motivate change. High reluctance towards anti-corrosion innovation is also fuelled by the length of the innovation cycle where long specification procedures require extended (accelerated) testing before qualification (time to market: >5 years). The associated efforts on the coating supplier side often multiply as no generally accepted qualification protocols for anti-corrosion solutions exist. Beyond obvious variations of the required routines between application cases, major differences between national authorities and major customer entities may exist and severely complicate the situation.

#### **3.3.4.2 Market opportunities and threats for the use of advanced coatings for aerospace, automotive and marine**

In contrast to significant technological reluctance to coating innovations, we observed high awareness to legislation issues both in Europe and in other core markets around the globe (USA, China). It induces a high implicit demand for preparation and quick adaption of possibly upcoming, expected, or even potential legislation throughout all industries (both coating

suppliers and end use). Here, we recognize a window of opportunity to attract industrial research and development efforts for coating innovations addressing supposed future replacement needs. Regulators, however, also need to consider adverse effects, where weaker environmental legislation could result in attracting industry to resettle at a location outside their effective reach. A foreseeable continuous long-term legislation process that carefully balances step-wise reduction of environmental impact and increasing technological capabilities appears desirable.

In general, current anti-corrosive coatings in passenger cars largely provide a sufficient cost-performance ratio. New market entrants in automotive coatings thus need their products to be especially cost-competitive, perform better and/or offer more functions than existing coating solutions. Within the next ten years, no major changes in car body materials and thus coating substrates are to be expected.

However, developing new anti-corrosive coatings for passenger cars may still pose financially beneficial market opportunities, as these are making for the largest growing segment in the automotive market [181]. Promising opportunities mainly concern the inner workings of the passenger car, such as the power train, engine, and the chassis, as well as small mechanical features like bonnet hinges and door latches. To exemplify, the lifetime of front break disks could be prolonged with a coating that is liquid repellent and simultaneously provides solid surface lubrication. Said coating would thus reduce corrosion of front break disks by preventing street dirt from sticking to them.

Other market opportunities do not necessarily include the use of graphene for corrosion protection, but for other purposes. Combining the high thermal conductivity of graphene with solid surface lubrication could serve for improving fuel efficiency and thermal management of cylinders in internal combustion engines. As to the car body, an opportunity for graphene lies within heating films, which would allow de-icing of the windscreen and LED headlight windows. In the emerging market of heating films and coatings graphene-enhanced innovations would meet less competition.

Main market opportunities for anti-corrosive coating and paint solutions for offshore wind parks lie within reducing maintenance hours of wind turbines, improving protection of mechanically stressed wind turbine parts, as well as improving paint technologies for areas inside the tower that are difficult to access.

New coatings could enhance the mechanical impact protection of wind turbine tower components and render manual coating of surface impairments due to wind turbine assembly unnecessary. Another opportunity lies within reducing wear and tear of wind turbine blades, as rain in offshore regions is especially abrasive to this component. Protective coating of areas as large, however, requires solutions to be especially cost competitive. Currently available solutions for large-area marine coatings and paints already are both low in cost per volume and of good long-term anti-corrosive performance. Addressing niche applications first would reduce competition. Graphene-enhanced formulations could improve mechanical

impact protection of wind turbine tower door area and flange area, which are mainly accessed during maintenance. When carried or applied, maintenance tools often cause coating impairments. Important is the possibility to combine or match such niche solutions with on-site application (such as manual spray-coating), which may be challenging with regard to paint gauge and dripping. Improving the paint application process or reducing coating gauge at same performance thus is desirable.

### 3.3.5 Innovation roadmaps

An explorative roadmap for a graphene enhanced coating for automotive, marine and aerospace application is presented below.

#### 3.3.5.1 Graphene for general coating applications

Significant technological development appears necessary (see above) before graphene can become a versatile additive material in coatings and coating systems in general. The insufficient maturity of the graphene industry today represents a core bottleneck hampering further development. Beyond the currently still prohibitive price level (that will eventually come down as soon as mass application takes place), challenges mainly relate to the inconsistency of graphene as a material class (lateral extent, layer count, contamination level, etc.) as well as a product (down to batch to batch differences from the same supplier). To enable successful implementation of graphene in various application fields, including coatings and coating systems, the graphene industry needs to improve their production processes continuously, establish reliable supply to their prospective down-stream markets, and harmonize product standards based on defining and agreeing on application relevant key performance indicators (KPI).

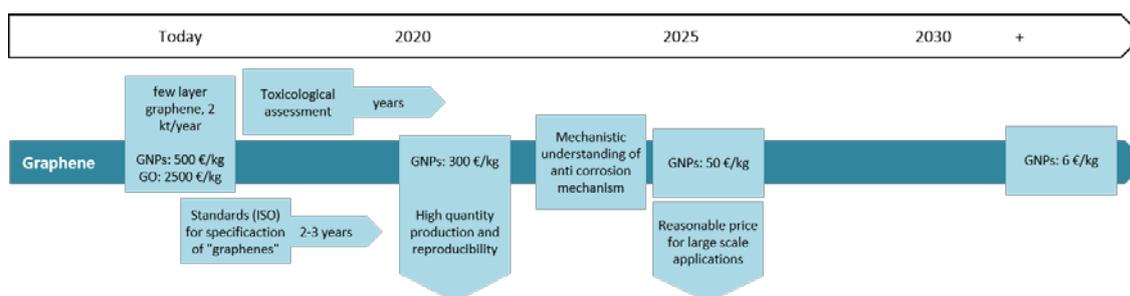


Figure 40: Roadmap for graphene production and development of materials suitable for coating applications.

In the field of anti-corrosion coatings, graphene may only one out of several active ingredients. Experts argue that coating stacks containing graphene in specific functional layers might be the best way to improve performance and meet cost requirements at the same time. In general, a cost range of 50 €/kg of GNP was considered achievable by 2025 and sustainable for large-scale implementation in the coating industry. Meanwhile, thorough toxicology assessment needs to provide solid evidence of the benign nature of graphene (in

the respective form), as ecologic issues of and following legislative restrictions on established anti-corrosion solution constitute a main driver for this specific application field. Beyond promising research results, the scientific community really needs to develop a mechanistic understanding of the anti-corrosion mechanism(s) induced by graphene: On the one hand, the knowledge will be required to tailor the actual coatings and coating systems to their application. On the other hand, the customer base of the paint industry simply demands a detailed understanding prior considering to employ novel products over established solutions.

### 3.3.5.2 Anti-corrosion coating suppliers

Innovation in the coating industry is mainly driven by new environmental legislation and further restriction expected down the road. Discussion often focusses chromate replacement, but other active ingredients play an important role, too, depending on location (regional/national) and application (market specific needs and rules). In general, it appears difficult for coating suppliers to change existing processes as they need to convince various customer groups to adapt a new material. Once the decision to implement a novel coating was made, scale-up tests will precede extensive prototyping to enable application specific qualification tests and, eventually approval of the novel coating product by the end-customer industries.

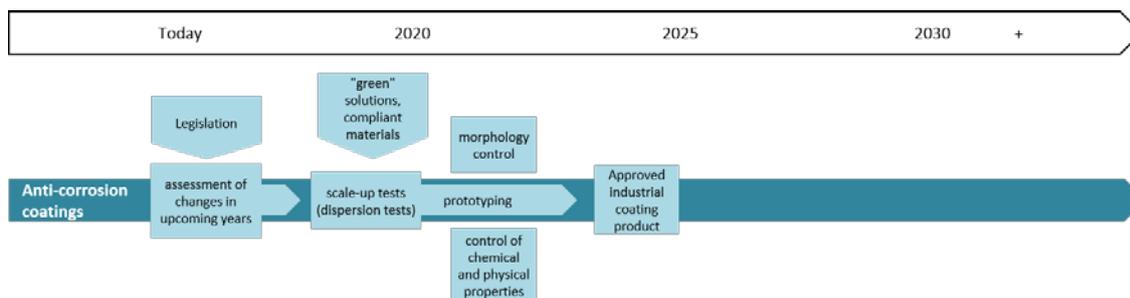


Figure 41: Roadmap for the development of new coatings.

### 3.3.5.3 Aerospace, automotive, and marine corrosion mitigation

Automotive, aerospace, and marine industries are typical examples of target markets for the coating industry to supply anti-corrosion solutions to. These actors will directly be affected by the regulation applicable to both their own (production) location and their own geographical target markets. Corrosion being just one of a multitude of aspects in their product development and marketing strategy, the industries remain extremely reluctant to switch from established processes to novel product – unless required by regulation, intrigued by superior quality and/or inferior cost, or enabling novel and distinguishable features for their products. In any case, the coating development and qualification process must comply with the industry-specific product development cycles.

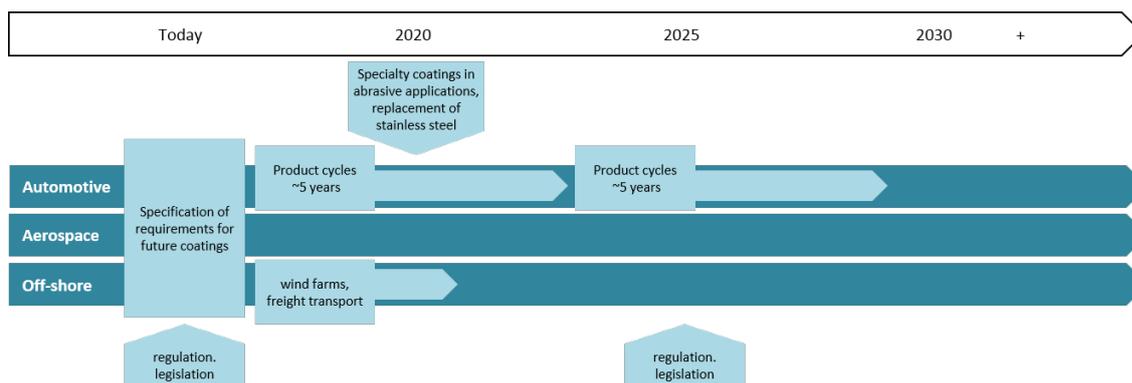


Figure 42: Roadmap for the application of new coatings in automotive, aerospace and marine industries.

### 3.3.5.4 Joint interface roadmap

Overall, regulation has been identified as the single most important driver for possible graphene application in the anti-corrosion sector. Specific discussion and requisites in the end user industry has to translate to an upstream information flow to prior stakeholder groups within the innovation chain. In open discussion of promises, opportunities, and drawbacks of graphene utilization in the anti-corrosion context, R&D in both graphene and coating contexts needs narrow down realistic application cases and foster the understanding of the underlying anti-corrosion mechanism(s). The successful adoption heavily depends on trust in the novel technology throughout the entire innovation chain. The introduction of reliable quality management and sufficient product standards constitutes an initial requisite for the graphene industry. Efforts regarding standardization and product comparability could potentially be supported by public authorities, e.g. in the frame of the Graphene Flagship.

Ramp-up of the production capacities and significant cost reductions of the graphene supply effectively first become relevant when its unique selling proposition for anti-corrosion has been established and verified in scale-up test by the coating industry. Decisions to engage in substantial efforts requires significant trust in timely cost improvement and supply capabilities. The actual product development then will require an extensive prototyping phase in which the coating industry will work in feedback loops with some of their respective clients on advanced functional and application testing. Once an approved industrial coating product has been established, final product qualification will usually take at least one typical product development cycle before implementation in any mass product.

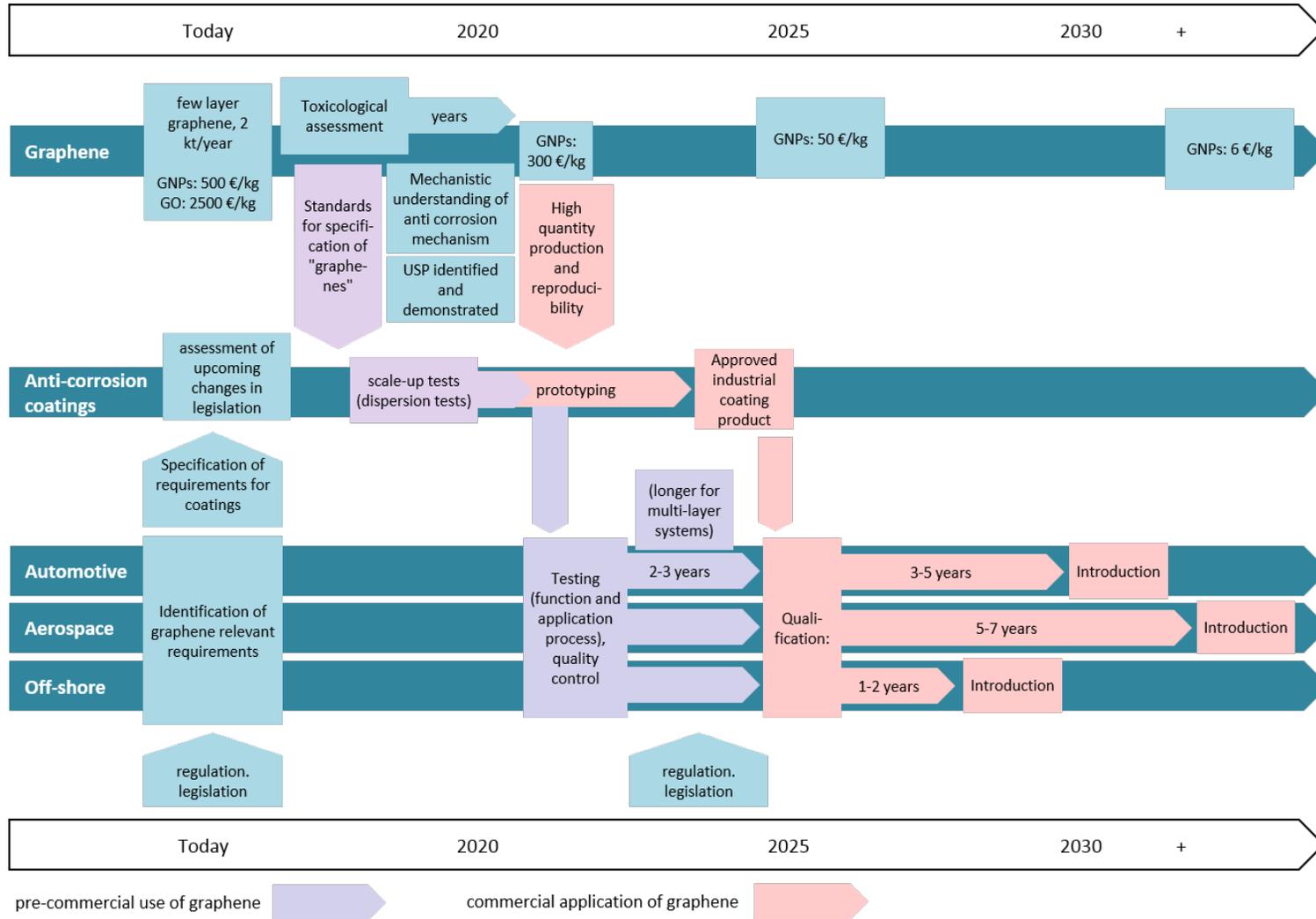


Figure 43: Interface roadmap for the introduction of graphene-based anti-corrosion coatings in automotive, aerospace and off-shore industries.

### 3.3.6 General conclusions on graphene-enhanced coatings

#### Status quo:

Coatings and paints cover a large variety of potential applications. Many potential niches and early adopters offer the chance for integration of graphene or other 2D materials. However, the vast amount of possibilities also induces a barrier for targeted research, as it is largely unclear where 2D materials actually can have a cost/benefit advantage. This is further amplified by the large amount of established coating technologies in the market, which introduce a barrier for new (nano-technology) coatings.

Besides, the following barriers/challenges are of additional importance.

- Often real proof of principle missing (tests only under artificial circumstances)
- Cost/benefit unclear
- Reproducibility and quality of the coatings
- Reliability and wear
- Environment, health and safety clarification
- Unclear optimal processes for targeted applications
- Anisotropy of conductivity properties need to be controlled

#### Opportunities for graphene:

Potential applications under investigation are anti-corrosion, anti-microbial, de-icing, or gas barrier coatings as well as thermally or electrically conductive coatings for electromagnetic shielding or against electromagnetic discharge. Again, the multi-functional properties are a rather unique asset of graphene materials.

2D materials are in principle the perfect coating materials, as they are ultimately thin films. Many potential applications are possible in form of both pastes/inks or as a neat (CVD prepared and transferred) film. The former has a lower implementation barrier, as inks and paints can be much easier applied with common available processes and are largely producible. 2D materials can be even added to common paints to improve properties (similar to composites). The challenges are the ink and paste formulation which needs to be targeted on the application and substrate. Functionalization can play an important role in this respect, but it is also much about choosing the right solvent and binder. Besides, the cost of the raw material is a smaller constraint, as for coatings smaller amount are usually needed. The process cost is therefore the limiting factor.

#### Requirements for successful market entry:

If the area of graphene/2D in coatings is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

The potential actions in the composite chapter also apply for coatings.

Besides, the following potential action relate to coatings:

- Evaluate lifetime under the targeted conditions
- Understand and investigate ink formulation
- Functionalization is critical (also on larger scale)
- Explore different applicabilities for different substrates, e.g. for textiles, foams, multi layered coatings etc.
- Demonstration! Also of wear and scratch resistance of coatings (use cases!!)

For all applications the cost/performance needs to be addressed and durability should be investigated from the beginning. Similar to composite materials, also the environment, health and safety properties and perception have to be considered.

### **3.3.7 Conclusions from Focus Research**

Corrosion causes significant damage throughout the economic system on a global scale. Thus, control and prevention of corrosion impacts implies huge markets for the paint and coating industry, but anti-corrosion solutions usually only constitute a minor side aspect at the end user level. Established and sufficient technologies usually exist, and end customers are highly reluctant to changes, but environmental impacts drive stricter regulation, abruptly enforcing transformation. Actors along the innovation chain anticipate upcoming change due to technical and regulatory developments. This creates opportunities for novel anti-corrosion solutions based on GRM once their functional principles were established and the efficacy of products verified. At present, a controversial discussion regarding anti-corrosion functions of graphene takes place in the scientific literature. Some consensus exists on beneficial barrier properties, but electro-chemical aspects remain highly disputed. Even in case clearer scientific results appeared, the paint industry would require improved graphene materials supply (see chapter 2) to engage in early upscaling tests. A sound mechanistic understanding of the underlying anti-corrosion mechanisms would not only support the product process, but also constitutes a key requisite for market entry as customers request convincing proof of long-term function.

## **3.4 Additive to liquids**

This chapter deals with the use of graphene/2D materials in liquids. It deals with the applications where the functionality of the 2D material is exploited in the liquid state. The major goal of these applications is the functionality enhancement of the fluids, e.g. enhanced electrical and/or thermal conductivity, better lubrication, etc. Typical products are lubricants and drilling fluids. In most of these applications, graphene competes with carbon black or other nano-carbons. This chapter does not cover applications where 2d materials are processed in liquid form but after application used in a solid (e.g. conductive inks, paints, coatings). The latter applications are covered in chapter 3.3.

Typical fluid applications where graphene or 2D materials can play a role are summarized in Table 18.

Table 18: Fluid applications for graphene or 2D materials

Type of fluid application	Functionality
<b>Lubricants</b>  Recent Review: [197]	<ul style="list-style-type: none"> <li>• Increased lubrication properties, reduced wear</li> <li>• modified electrical conductivity for lubrication of electrical contacts or isolation</li> <li>• thermal conductivity for better heat removal</li> <li>• impede corrosion</li> </ul>
<b>Adsorbent for polluted liquids/water, contaminant adsorber</b>  Recent review: [198, 199]	<ul style="list-style-type: none"> <li>• Oil spill clean-up</li> <li>• Hydrocarbon/pollutant binding and removal</li> <li>• Metal ions and organic compound adsorbent</li> <li>• Photocatalytic, disinfectant and adsorbent with metal oxides [200]</li> </ul>
<b>Drilling fluids [201]</b>	<ul style="list-style-type: none"> <li>• Better lubrication, reduced wear</li> <li>• Better heat removal</li> <li>• Reduce losses of drilling fluid to surrounding rock</li> <li>• Thinner, lighter filter cake</li> <li>• Improved well logging (needs conductivity in the fluid)</li> </ul>

This chapter also covers the special case where graphene material powders are used for environmental remediation in fluids, e.g. for oil spills (Directa Plus) as an adsorbent for polluted liquids/water. The graphene materials directly compete with other (carbon-based) materials that can be used for hydrocarbon removal and oil spill clean-up.

### 3.4.1 Market perspective: graphene/2D in liquids

Depending on the use, the percentage of additives in lubricants varies between 0.5% and 30%, e.g. for steam turbines or compressors 0.5% and 5% or for hydraulic systems 2% to 10%, for engines 10-30% of additives are added. The types of additives are specific for specific applications [202, 203].

The lubricant additives market is expected to grow at a rate of CAGR 2.7% over the next years to reach \$16.2 billion by 2019 (~\$14.2 billion in 2014). The growth is attributed to a high demand from major end-use industries such as construction, automotive, and manufacturing. [204, 205] The value of lubricant additives produced in Europe in 2014 was €4.7 billion, growing at a CAGR of 7.9% 2012-2014 (lubricants itself: €2.4 billion,

stagnating 2012-2014), with an average unit value of ~2-2.8€/kg in 2014. Thus, European companies have a large and growing share in this additive market.[155]

The overall lubricants market was estimated to \$ 144.45 Billion in 2015 and is projected to reach USD 166.59 Billion by 2021, (CAGR of 2.4%). [206] European companies have a small share in this market and are rather suppliers of additives.

The global market for drilling fluids is expected to reach >\$14.5 billion by 2020. The global market for drilling fluids was estimated to be ~\$8.16 billion in 2013, and is expected to grow at a CAGR of ~7-8%, dominated by America and Asia Pacific.

56% of the total market revenue in 2013 was created with water based fluids, the most consumed drilling fluids. They are also expected to have the fastest growing demand (CAGR of almost 9% from 2014 to 2020). Oil-based fluids are the second most used for drilling, accounting ~30% of the total market 2013. Major companies come from US, only a few multinationals are in Europe (Schlumberger). [207, 208]

The global market for technologies used in the remediation of environmental contamination of surface water, groundwater and soils was estimated at ~\$60 billion in 2013. It is expected to grow from ~\$61.7 billion in 2014 to ~\$80 billion in 2019, (CAGR 5.5%). China is expected to more than double their total market share from 4.7% in 2014 to 10.8% in 2019. The Latin America and Caribbean region could also see stronger growth than average expanding its market share to 7.8% in 2019. The rest of the market is dominated by the most developed economies of North America, Western Europe, Japan and Australia [209]

The global adsorbents market was estimated to be ~\$3.1 billion in 2015 and is expected to reach ~\$4.3 billion by 2020 (CAGR 6.3%). This growth is fuelled by the increasing global demand for petroleum refining, chemicals/petrochemicals and gas refining industries. A high potential is attributed to molecular sieves and activated carbon. [210]

### **3.4.1.1 Market Opportunities**

#### **3.4.1.1.1 Increased need for high performing and sustainable lubricants**

The overall need for lubricants is to increase the lubrication and reduce wear. The increased use of robots and the need for energy efficiency calls for better lubrication and multi-functionality. On the other hand, long term automotive trends (electromobility) will change and decrease the demand for lubricants. In medium term, the demand for reformulated, higher-performing lubricants increases due to downsized powertrains.

Another need is to increase the multi-functionality of lubricants, i.e. to increase the thermal conductivity of lubricants for heat removal or to use lubricants for electrical contacts

that support the contact by reducing contact resistance. Similarly, other applications need improved electrical or thermal insulation.

There are also special applications where specialty lubricants need to withstand chemical environments, low temperature, radiation or vacuum. Additives in general are used as friction modifiers, antioxidants, corrosion inhibitor, detergent/dispersant, for anti-wear, anti-foam, alkalinity improvement, demulsification, extreme pressure performance, chemical resistance or viscosity.

A successful integration and increased performance opens up many potential markets, as with additional functionalization many needs could be addressed.

#### **3.4.1.1.2 Strength of European lubricant additive manufacturers**

Europe has a competitive and strong lubricant additive supplier industry, which could be further enabled by 2d materials. However, the lubricant manufacturers themselves are rather under-represented in Europe. The competition is moderate, in particular for high performing lubricants.

#### **3.4.1.1.3 Tightened laws on pollution and increased need for remediation**

In particular in Europe, but also globally, tightened laws on pollution and clean water increase the need for remediation, e.g. of surface water and waste water from oil production.

### **3.4.1.2 Market Threats**

#### **3.4.1.2.1 High price sensitivity of conventional lubricants**

Conventional lubricants are subject to a rather high price sensitivity (~1-2€/L). Lubricant additives cost around 2-3€ on average per kg. Even if the loading can be reduced through the use of graphene/2D materials (typical loadings are between 0.5 and 30%), the price pressure will still be high for mass markets. It is important to address the systemic cost balance (e.g. lower total maintenance and/or energy costs), as a higher performing and more durable lubricant for instance needs to be changed less often, allowing a higher price.

On the other hand, there are also special markets with particular needs for high-performing lubricants or specialty lubricants allowing higher prices.

#### **3.4.1.2.2 Mature and established competing products**

The lubrication additives market is well established and many additives exist that allow proper modification of lubricants. Organo-metallic compounds, polymers, phosphorous or sulphur compounds, aromatic compounds, but also MoS<sub>2</sub> and graphite are used. [211]

For remediation and oil spill cleanup, many other (carbon based) sorbent materials are available. The same is true for drilling fluids.

A new additive needs to improve the cost/performance significantly and undoubtedly to allow uptake in industry.

#### **3.4.1.2.3 Environment, health and safety requirements**

The need for sustainable lubricants, drilling fluids and adsorbents is increasing. Sustainability is increasingly important and needs to be proven. This includes end-of-life properties (e.g. recyclability), environmental safety as well as health and safety (release of graphene, contact with graphene) considerations. These issues have to be addressed to avoid misperceptions and bad publicity.

Toxicity is seen as a severe problem in additive technology, because real long term biological and ecological effects are mostly not known. [212]

It can be expected that in areas with no tradition of protection against harmful substances, industry will be reluctant to use graphene materials. This is particularly relevant where graphene-based formulations are to be released into the environment or to be used in workplaces (e.g. many lubricant applications). Use of fluids inside closed industrial processes, however, are more probable.

### **3.4.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in liquids**

#### **3.4.2.1 Current strengths of graphene/2D materials use in liquids**

##### **3.4.2.1.1 Functionalization and multi-functional property enhancement in lubricants and drilling fluids**

Similar to the other applications, again the multi-functional property enhancement is the largest asset for graphene materials as additives to fluids. For lubricants, the combination of electrical/thermal properties and lubrication are of high interest. This also applies to drilling fluids.

Similar to graphite, graphene possesses good intrinsic tribological properties on the nano-scale. When used in oils, graphene platelets and GO show slightly better friction coefficients than graphite and a reduced wear [197].

Also other 2D materials such as MoS<sub>2</sub>, WS<sub>2</sub> (and other TMDs) or BN are of interest, in particular because they are already used in lubricants. Recent studies have shown that MoS<sub>2</sub> nanoplatelets increases the performance under pressure and high load conditions compared to other additives. [213] This enhancement of standard lubricant additives by

turning them into 2D materials (such as  $\text{MoS}_2$ ) could pose a rather easy implementation and a low barrier, if performance improvements can be shown.

Due to the possibility of functionalization, the properties can be adjusted and the diversity is increased. However, functionalization also has some drawbacks, see 3.4.2.2.1.

#### **3.4.2.1.2 High specific surface area and functionalization for remediation**

The high specific surface area of GO allows a high adsorption rate for hydrocarbons in oil spill clean-up. This eventually leads to a higher adsorption capacity and less needed material. A potential uniqueness is also the hydrocarbon removal at low concentration. [97, 214, 215]

Due to functionalization, the properties of GO can be tuned so that it becomes hydrophobic and oleophilic, the prerequisite for oil spill cleanup and highly polluted water cleaning (e.g. from oil drilling).

The chemical inertness, thermal and mechanical stability also allows recycling and recovery of sorbent and adsorbent.

#### **3.4.2.1.3 Nano-graphite/graphene platelets and GO are sufficient: Low implementation barrier**

For the additive to liquids application, usually graphene/2d platelets, GO or even exfoliated graphite/nano-graphite is used and sufficient. Therefore, the implementation barrier is low, material availability is there and the application has a rather high maturity and expected short time to market (for graphene, not other 2Ds). However commercial viability and cost/benefit still needs to be proven (see 3.4.2.2.2).

Besides, addition to liquids can be seen as a by-product of coatings or composites, where also the graphene/2D platelets need to be dissolved/dispersed. The benefit of a liquid is that it is used as it is and does not need to be applied or dried or further processed. This also reduces the implementation barrier.

### **3.4.2.2 Current weaknesses and challenges of graphene/2D materials use in liquids**

#### **3.4.2.2.1 Unclear influence of surfactant on properties and stability of dispersion**

The surfactant or functionalization which is needed to keep the 2D materials dispersed can have negative effects on lubrication or adsorption properties. The most important challenge is to find a functionalization that enables a stable dispersion and long term stability in dispersion (e.g. to survive storage and transport) and at the same time resembles the needed functionality. In that respect functionalization is boon and bane, as it

opens up many possibilities, but also constitutes many different approaches and a high degree of freedom with many possibilities, which can also be disadvantageous when looking for the right functionalization. Besides, most functionalization protocols are today available at rather small scale.

In particular for oil spill cleanup applications, the hydrophilicity of (pristine) GO needs to be reversed to hydrophobicity and oleophilicity through functionalization.

#### **3.4.2.2.2 Cost/benefit needs to be proven**

Similar to most of the bulk applications of graphene or other 2D materials the cost/benefit is not yet clear and needs to be proven. There are promising lab results which need to be transferred to real applications.

For liquid applications, it needs to be proven whether the benefits outweigh the potentially added costs. For instance it needs to be shown that for oil spill cleanup GO reaches a higher cost efficiency than other sorbents.

For lubricant additives there are no rules up to now to predict additive performances at a given technical application. As a consequence formulations have to be tested and forecast extensively to assure the functionality. Such testing is addressed by international and national regulations. It is further important to look at the lifecycle cost, as a longer lasting lubricant can potentially cost more than a lubricant that degrades earlier. Therefore, added costs can be justified by added functionality if the life cycle costs remain lower (e.g. due to use of lower amount of lubricant, less often change of lubricant, less wear of lubricated parts)

#### **3.4.2.2.3 Clarification of toxicology/biocompatibility**

In particular for use of graphene in open waters, drilling holes and in the environment, the toxicology and biocompatibility of the used form of graphene needs to be broadly tested.

The biocompatibility depends on the type of graphene (e.g. oxygen content, lateral size). For use as oil spill cleanup especially endocytosis needs to be investigated. It appears that current results are "optimistic" in terms of biocompatibility in this respect.

For lubrication applications standard health & safety and regulatory classifications have to be conducted. The eventual fate of graphene and composites used as adsorbent needs to be investigated

### 3.4.3 KPIs for liquids

#### 3.4.3.1 Lubrication

- Tribological properties: Friction, wear rate (also under pressure/heavy loads, temperature), lubricity
- Viscosity, viscosity index
- Pour point
- Flash/fire/autoignition point
- Chemical stability
- Oxidation and corrosion stability
- Thermal conductivity
- Electrical conductivity
- Cost per volume
- Recyclability/End of life properties

#### 3.4.3.2 Remediation

- Absorption capacity: Absorbed material per g of adsorbent
- Absorption rate
- Absorption rate and capacity, as well as concentration reduction depending on conditions (temperature, concentration of material to be absorbed, type of material absorbed)
- Hydrophobicity (water contact angle)
- Efficiency of recovery/recycling of adsorbent (reusability, effect on other KPIs after cycles)
- Toxicology/environmental sustainability
- Life cycle cost

### 3.4.4 Roadmap for liquids

#### 3.4.4.1 Current maturity: Drilling fluids on the market, remediation and lubrication under investigation

Additives to liquids have a rather high maturity and expected short time to market, because the integration is rather simple and the application can be seen as a by-product of graphene flake integration into composites.

There are already marketed products (Graphene Nanochem drilling fluid) and plans or concrete investigations to market products (remediation/oil spill cleanup: Directa Plus, lubrication: Puralube [216]). Most of the efforts are technology push driven.

In terms of functional lubricants (e.g. thermally conductive), the maturity is rather low and on lab scale.

### **3.4.4.2 Barriers/challenges (summarized)**

Main challenges are

- actual demonstration of cost/benefit and performance increase towards competing technologies and state of the art
- scalability of processes (e.g. functionalization)
- shelf life of dispersions
- Unclear environmental properties, in particular for oil drilling fluids and remediation
- Functionalization (find the right one and scalable)

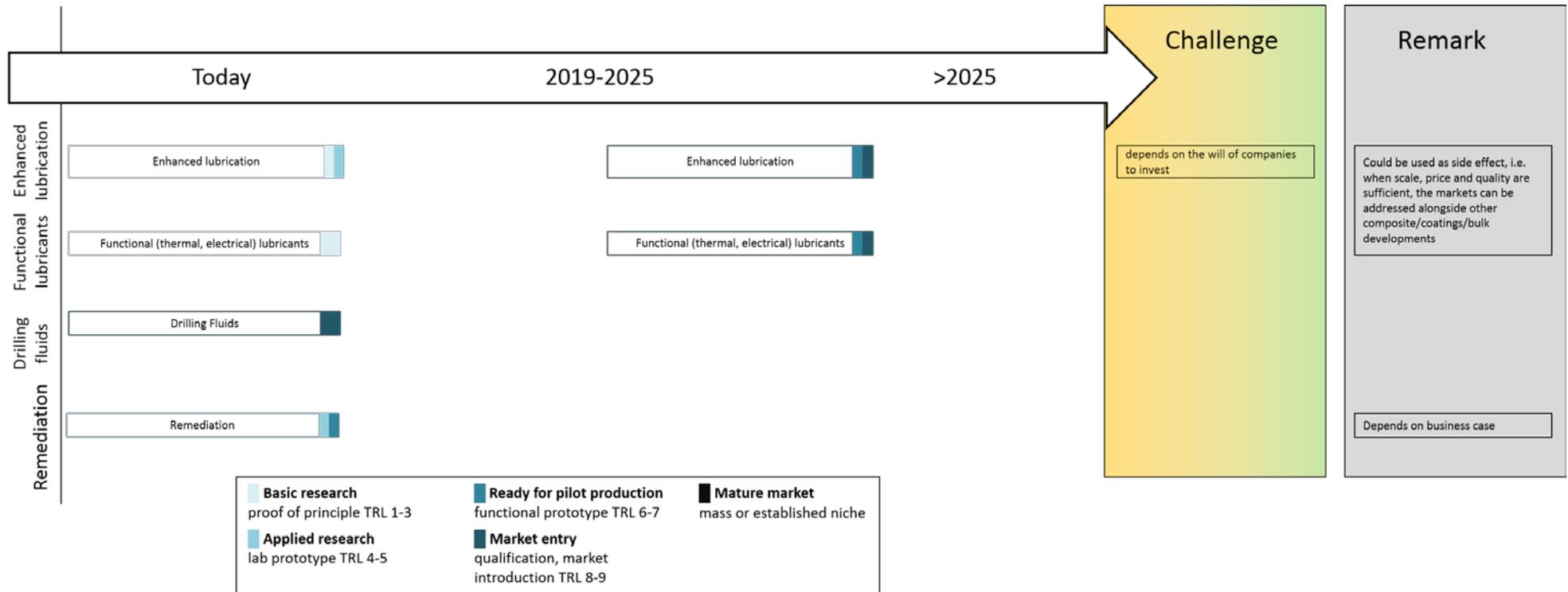
### **3.4.4.3 Potential actions**

If the area of graphene/2D as additives to liquids is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

As additives to liquids can be investigated alongside composites, similar actions are required (such as large scale functionalization). In particular, the application oriented testing needs to be further pursued:

- Application oriented testing under realistic conditions
- Testing of other 2D materials
- Investigate large scale functionalization
- Prove/investigate environmental sustainability
- Investigate end of life properties
- Life cycle cost assessments

### 3.4.4.4 Roadmap



### 3.4.5 Conclusion for liquids

Adding graphene or 2D materials to liquids, such as oils or water is straight forward, as long as the functionalization is right. Essentially, the use in liquids has a lower implementation barrier as coatings or composites, due to the fewer steps needed for implementation. The use in liquids can therefore be seen as a byproduct of coatings or composites. Furthermore, simple to produce graphene varieties can be used, such as GO.

Again, the multifunctional properties are the greatest selling proposition, e.g. electrical and thermal conductivity plus increased lubrication. This is, however, not fully explored yet and the cost/benefit is not clear.

For remediation and oil spill cleanup the high specific surface area is of interest. However, the overall cost/benefit towards other (carbon-based) adsorbents. Besides, for the broader use in the environment, the environmental friendliness needs to be approved.

There are already first graphene-based products on the market, e.g. drilling fluids from Graphene Nanochem and there is the effort of Directa Plus to commercialize their graphene material for oil spill cleanup. There are also first lubricant manufacturers observing the use as an additive (e.g. Puralube).

Table 19: Assessment of market and technological potential of graphene/2D materials use in liquids on a scale - , -, 0, +, ++

Application in fluids	Current technological potential (USP)	Market potential (EU perspective)
Lubricants (wet)	0	+
Adsorbent for remediation	0	0
Drilling Fluids	0	-

### 3.5 Special application: Filtering, desalination/deionization and membrane applications

2D materials are the perfect candidates for membranes: ultimately thin, strong and modifiable through functionalization and manipulation. This chapter covers the use of graphene/2D materials as membranes in general and also as a coating or additive to membranes or filter materials for (water) filtering and desalination (membrane and capacitive deionization) [217]. Typical applications are presented in Table 20.

Table 20: Potential applications of graphene and 2D materials in filtering, desalination/deionization and membrane applications.

Type of application	Functionality	2D material
Membrane Review: [199, 218–221]	<ul style="list-style-type: none"> <li>• Water treatment, filtering (reverse or forward osmosis)</li> <li>• Separation and filtering of liquids or gases</li> <li>• Filtering, size selection of nano-materials</li> <li>• Sensing, DNA sequencing [222]</li> <li>• See also 0</li> <li>• Fuel Cells and hydrogen economy for potential applications</li> </ul>	Graphene, rGO, GO
Electrode for capacitive deionization (CDI) [199, 217, 223]	<ul style="list-style-type: none"> <li>• Replace activated carbon</li> <li>• High surface area, High ion-accessible surface area, high salt adsorption capacity, high adsorption rates and (electro)chemical stability</li> </ul>	rGO, GNP
Coating [199, 220, 221] <i>Also see chapter 3.3</i>	<ul style="list-style-type: none"> <li>• Anti-fouling, anti-bacterial, hydrophobic, auto-clean, enhances water permeability of standard (polymer) membranes</li> </ul>	GO
Additive to membrane materials [199, 221] <i>See also chapter 3.2</i>	<ul style="list-style-type: none"> <li>• Reinforcement, durability</li> <li>• Functionality (e.g. conductivity, anti-fouling)</li> </ul>	GNP, rGO, GO

The graphene-based technologies range from GO-based layered structures as membranes, GO addition to polymeric membranes (as additive or coating) to enhance water permeability and address anti-fouling (G2O [224]), graphene as a perforated membrane itself used like a molecular sieve (Lockheed “Perforene” [99], CNM Technologies [225]). In terms of water desalination, these technologies are investigated for forward or reverse osmosis. But the actual graphene membranes can be also used to size selectively filter, even to separate heavy water (D<sub>2</sub>O) from water (H<sub>2</sub>O) [226], CO<sub>2</sub> Capture (chemical functionalization needed) [225] or for DNA sequencing, where also the electrical properties are exploited [222].

Besides these functional properties, graphene materials can also be used to increase the mechanical properties of membranes. Here the same considerations apply as presented in chapter 3.2.

Graphene material can be also used in capacitive deionization (CDI) for water desalination, an alternative technology to reverse osmosis. In this technology, the performance depends strongly on the electrode, which in current configurations is made from activated carbon. The general idea is to replace this by graphene to improve the performance and diminish the energy consumption.

### **3.5.1 Market perspective: graphene/2D in filtering, desalination/deionization and membrane applications**

The market needs for the improvement of membrane and filtering technologies are to filter correctly, increase the lifetime and decrease maintenance efforts, improve self cleaning properties and reduce effort for cleaning cycles, reduce energy consumption. Desalination/deionization has the same needs, but in particular increased throughput and reduced energy consumption are crucial aspects. The market needs for the improvement of CDI technology are suitable electrode materials with high electroadsorption capacity and high adsorption rate to improve the performance and reduce the energy consumption.

The global membranes market is projected to grow at a CAGR of ~9.5% from more than USD 20 billion by 2015 to USD 32 Billion by 2020. Asia-Pacific and North America are the key markets for membranes. High growth is expected in Middle East & Africa and Latin America. The market is mainly driven by water & wastewater treatment, pharmaceuticals & medical uses (together 62% market share), food & beverages, and chemical processing sectors. Industrial gas processing segment is projected to witness the highest growth rate due to increasing use of membranes in the oil & gas sector for gas processing, hydrogen production or carbon dioxide removal from natural gas streams.[227]

In terms of the European industrial basis, the revenue created with water and gas filters and filter equipment/machinery was €14.4 billion in 2014 (CAGR 4.6% 2012-2014), of which €2.5 billion were parts for filtering and purifying machinery for liquids or gases (CAGR 4.6% 2012-2014).[155] The global market for the filter industry was \$59.1 billion in 2013 and a CAGR of 6.2 percent to \$80.0 billion in 2018 is expected.[228]

Looking at transnational patents (Figure 44), the field is dominated by applicants from the US. China is emerging in recent years, but European actors are also at a similar level.

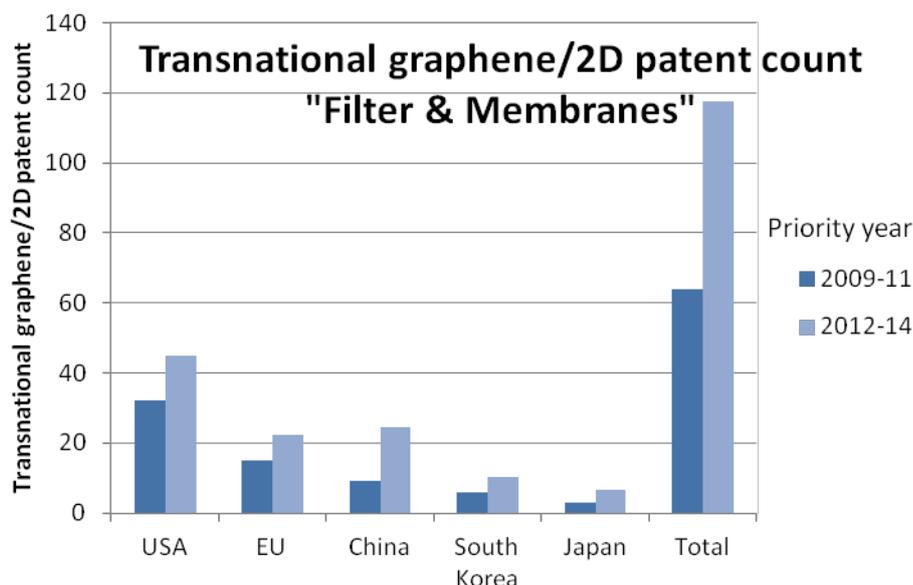


Figure 44: Patent analysis of graphene/2D materials in filter and membranes: Number of graphene related transnational patents in 2009-2011 and 2012-2014. 2012-2014 values are projected. [137]

The relevance of graphene in membranes and filters (the ratio of graphene/2D patents from all patents in the area) is depicted in Figure 45. It is increasing strongly. In particular in China and Korea there is a stronger focus on graphene/2D materials in filters and membranes. Although the total count of patents is higher in Europe and the US.

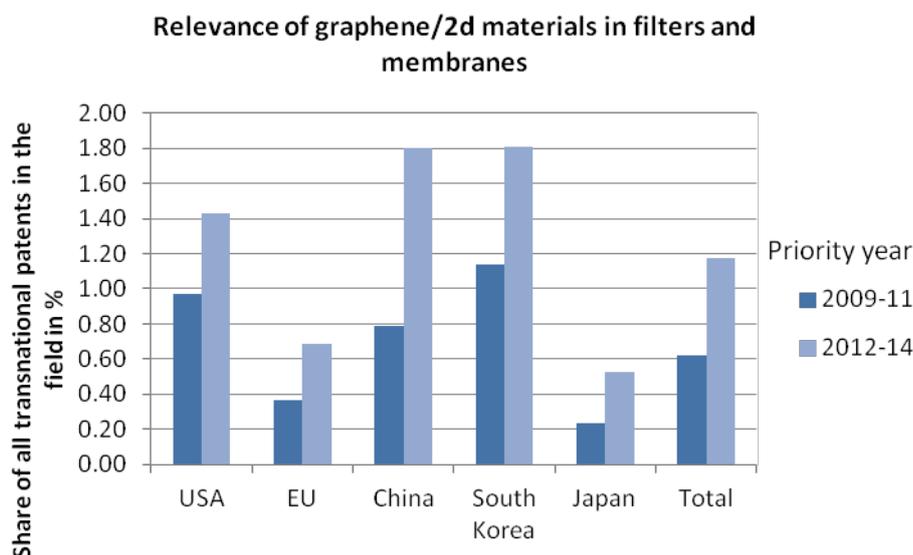


Figure 45: Patent share of graphene/2D related materials with respect to all transnational patents in filters and membranes. 2012-2014 values are projected.[137]

### **3.5.1.1 Market Opportunities**

#### **3.5.1.1.1 Increasing need for fresh water**

Global climate change; global warming and increasing population increase the pressure on the water system. Water scarcity and increasing water stress leads to additional demands for fresh water technologies: through 2050, additional 2.3 billion people are expected to be living in areas with severe water stress, especially in North and South Africa and South and Central Asia [229]. The world could face a 40% global water deficit by 2030 under a business-as-usual (BAU) scenario.[230]

On the other hand, the need for portable water will exist due to a lack of infrastructure. Portable or smaller water treatment or desalination equipment could address this problem. This all leads to an increased need for resource efficient water treatment and an increasing need for water desalination with low energy consumption and low maintenance. The past five years has seen a 57% increase in the capacity of desalination plants. [231]

The increasing regulation on water quality in Europe and worldwide also drives the need for more energy efficient treatment technologies. This is not only affecting large scale plants, but also small scale treatment systems, e.g. the increasing need for hospitals water treatment.

Groundwater decontamination in the developing world is also a large market with unmet needs. Besides, applications as resin based water softener replacement or water treatment for cooling towers may also be attractive applications. CDI may very well address those markets.

#### **3.5.1.1.2 Weaknesses of common technologies in desalination**

Desalination gains importance but still is very energy intensive, even the most advanced reverse osmosis (RO). The constraints of RO are: low water flux and salt rejection, membrane fouling and regular membrane replacement.[220] Major trends are the reduction of energy consumption and improvement of self cleaning solutions. Additionally, current fresh water and desalination systems are usually large plants because of the economy of scales. Novel technologies can also enable more decentralized and mobile systems that allow a broader and more flexible supply without the need for extensive infrastructures or logistics.

One of the promising, mature but underperforming technologies is capacitive deionisation (CDI). Benefits of this technology is the absence of applied pressure, high rejection of salt, more efficient for low salinity feed water sources (TDS < 15,000 mg/L) and a much higher water recovery (up to 90% or more) than RO, which normally has a recovery

rate of 50% or less. Additionally, a polarity reversal results in self cleaning of the electrodes.[219] The overall energy consumption of 0.1–2.03 kWh/m<sup>3</sup> is lower than for RO (3–6 kWh/m<sup>3</sup>).[217] CDI in the short term, is expected to be used for low salt concentration water such as underground water (<5,000 ppm TDS) and not for sea water due to high CDI unit costs. The expected cost of desalination using current CDI technology is 0.36 \$/barrel for this lower TDS (total dissolved solids) water, which is much less than reverse osmosis (6.11 \$/barrel) and membrane electrodialysis (5.5 \$/barrel). [232]

However, the efficiency of electrodes for salt separation requires optimization.[219] Standard materials are activated carbon, which is not selective and an optimum electrode was not yet found. The performance strongly depends on the electrode material. There is furthermore only limited data for seawater desalination available.[219] CDI also suffers from the requirement of a considerable external power source and the issue of brine solution disposal of the system. Furthermore, the electrode suffers from self contamination depending on the source water.[217] The market needs for the improvement of CDI technology are suitable electrode materials with high electroadsorption capacity and high adsorption rate. The NaCl adsorption capacity of the currently carbon-based materials is in the range of 0,1–10 mg/g, which is much lower than the theoretical estimations, leading to a too low performance.

#### **3.5.1.1.3 Many other filtering/membrane opportunities**

Besides water desalination or purification (waste water treatment, CDI), filter materials and membranes are also important in (exhaust, process) gas cleaning and separation, industrial and pharmaceutical material production/purification processes and analytics. These markets offer highly specialized needs that can be addressed by new technologies. Early adopters are available in this respect, especially for harsh conditions.

Membranes can be seen as a platform technology with a variety of potential end products. If the technology is understood and controllable, more potential markets arise.

#### **3.5.1.1.4 European strength in filter and filtering equipment**

With a production value of €14.5 billion in 2014, the European filter industry is rather strong and potential integrators are in Europe. [155]

Furthermore, the competition on the market, especially for high quality products is rather moderate, although the competition increases. Besides, the patent activities (Figure 44) suggest that Europe is not leading this technology strand in terms of graphene and 2D materials, but has a reasonable share of activities. Besides, Europe has the highest overall patent share in this area (independent of graphene/2D), suggesting a strong and innovative industrial backbone (see Figure 46).

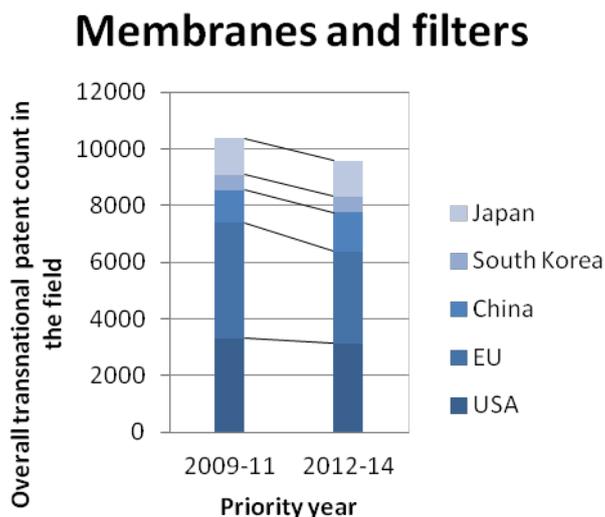


Figure 46: Overall transnational patent count in membranes and filters. 2012-2014 values are projected.[137]

### 3.5.1.2 Market Threats

#### 3.5.1.2.1 High quality standards and cost sensitivity pose market barriers

Especially the fresh water markets pose barriers due to high standards in terms of durability or health and safety, whilst being cost sensitive. Typically, the markets allow only smaller cost increases for improved functionality or performance on system level. The cost-benefit is usually addressed on system and life cycle level, where the latter eventually needs to be lower. But in terms of added cost for membrane and materials, the room is very limited: The module prices of filter cartridges depend on many different components and membrane materials comprise only a small component of the module price. As they comprise currently a rather small portion of the price, large increase is not possible.

In general, durability needs are high and need to be addressed. A new technology is only feasible, when it is durable and requires low maintenance and down times. A non-negligible issue is that proving durability is rather tricky. Despite accelerated testing, in a conservative industry one will mostly use the technology that actually has shown its durability in commercial applications.

Currently, the need for lower energy consuming technologies is also curbed because of the low fossil fuel prices.

### **3.5.1.2.2 Competing materials and technologies are diverse**

In terms of desalination reverse osmosis is currently the dominant and most economically effective technology. There are also several older plants based on thermal desalination.

In terms of membrane materials, also other emerging materials pose promising properties, such as Zeolites, CNT, Silica, TiO<sub>2</sub> and silver nanoparticles and thin film composites (TFC).[220] Clear benefits in terms of functionality or performance need to be shown towards these technologies and the state of the art.

## **3.5.2 Graphene/2D materials perspective: Current strengths, weaknesses and challenges for the use in filtering, desalination/deionization and membrane applications**

### **3.5.2.1 Current strengths for graphene/2Ds materials use in filtering, desalination/deionization and membrane applications**

#### **3.5.2.1.1 Ultimate membrane: selectivity, mechanical strength and pore size**

As a 2D material, graphene has ultimate membrane properties and very small pores are possible. This allows size and ion selective filtering and can be also used for sensors and science (chromatography-like).

Additional functionalization allows tuning of further properties and selectivity. Interest from industry is there (e.g. Lockheed Perforene) and expectations are [99]:

- Tolerance towards harsh conditions (temperature, pH, chemicals)
- Higher permeability (two orders of magnitude)
- Hydrophobicity reduces fouling

For desalination, the expectations are to increase the membrane flux by a factor of five with fewer required elements, which translates in 10-20% energy consumption due to lower needed pressure and 80% fouling reduction and correspondingly enhanced membrane life.

#### **3.5.2.1.2 Laminates as a possible simpler use in membranes**

GO graphene laminates (water transport through capillaries) depict a simpler use of graphene materials as membranes. The exhibit good mechanical properties, fast water transport and high rejection capability. The membranes can be tuned to be ion selective. [219] The production and implementation of these membranes is potentially easier as for single layer membranes.

### 3.5.2.1.3 Interesting enhancements for polymer membranes

Graphene platelets and graphene oxide can be used to enhance the functionality and mechanical strength of polymeric membranes as an additive or as a coating. Added functionalities are hydrophobicity, anti-fouling, anti-bacteria, auto-clean, higher water permeation. The enhanced membranes are ultra-permeable and the GO enhanced membranes show significantly improved membrane performance and anti-fouling. [220, 221]

With the variety and possibility of functionalization the properties can be further tuned. For mechanical enhancement, see chapter 3.2 for further considerations. The goal is to increase the lifetime of filters.

This application poses a rather low barrier, as integration is comparably simple and the state of the art technology is just slightly modified. 2D materials can be used as any other additive and the form factors and outline of the membrane does not change, so the system itself does not to be changed as well.

### 3.5.2.1.4 CDI: Potential enabler

CDI electrodes need high ion mobility, high adsorption capacity (which is related to the surface area and pore size) and low electrical resistivity, all addressable with graphene. Currently mesoporous (activated) carbon aerogels are used with specific surface areas of 400-1100 m<sup>2</sup>/g and electrical resistivity of less than 40 mΩ cm. [219]

The unique selling proposition of graphene materials is the higher specific surface area combined with the electrical conductivity, chemical properties and the possibility to be functionalized. Currently, reduced graphene oxide is investigated. The chemical properties and potential variety of functionalization could be exploited for better selectivity for ions or molecules due to the much more controlled surface. High surface area and porous electrodes can be achieved by using three-dimensional reduced graphene oxide, with macropores, to enhance the ion mobility and ion accessibility; and micropores for high adsorption capacity. The mobility, capacity and hydrophilicity can be further enhanced by addition of metal oxides nanoparticles. Graphene materials are rather unique material candidates for improving CDI.

Graphene electrodes reach an ion removal efficiency of 18.5 mg (ions)/gram (electrode) [233] while activated carbon electrodes are between 2-5 (ions)/gram (electrode) [223]. It can therefore enable the use of CDI also for higher TDS (total dissolved solids) water.

### **3.5.2.2 Current weaknesses and challenges for graphene/2D materials use in filtering, desalination/deionization and membrane applications**

#### **3.5.2.2.1 Membranes: maturity and unclear actual performance [217, 219, 220]**

The current experiences are to a great extent based on lab scale experimental results and modelling/simulation studies. For water desalination, actual tests, e.g. in reverse osmosis configuration, are not yet performed. The membranes need to be optimized to be functional and effective in high pressure configuration under real conditions.

Therefore, important knowledge for an objective application assessment of real-life chances that graphene can be used are missing: recovery range, feed water quality (at least seawater salinity is a must), energy consumption, cost impacts. In terms of energy consumption, expectations are that it will be similar to common RO membranes. Cost will depend on the ability to produce the right quality and quantity of graphene and the integration into membrane structures.

For actual graphene membranes (e.g. perforene), a main weakness is the trade-off between water flow and mechanical stability: a higher flow requires more pores, which reduced the mechanical stability. The optimal pore distribution also needs to be found.

Besides the potentially needed exact membrane nanopore fabrication is a challenge, e.g. for DNA sensing, where pore sizes need to be very precise.

#### **3.5.2.2.2 CDI: Unclear cost/benefit and current maturity in CDI**

For the use in CDI, the potential is large. However, the experimental validation is still open. There are only lab scale CDI tests available and no reproducible proof of an improved effect are available yet. The important question is, whether the cost/performance will be good enough to become dominant technology compared to activated carbon. Only if the improvement is considerably high, higher costs are justified. For moderate improvements, the costs for an upgrade from activated carbon to graphene might become too high.

#### **3.5.2.2.3 Health and safety for drinking water needs to be addressed**

As graphene is a nano-material, health and safety need to be addressed from the beginning, in order to avoid the threat of health concerns (see 3.5.1.2.1). In particular for desalination and drinking water applications, health and safety needs to be proven. For instance, aging studies can be performed on GO-based CDI electrodes in order to evaluate GO release and thus health and safety.

### 3.5.3 KPIs for filtering, desalination/deionization and membrane applications

- Compatibility with environment and regulation (no release of graphene)
- Pressure/operating conditions
- Permeate flux
- Rejection and selectivity of filtering
- Durability, reliability and contamination/fouling
- Recovery
- Energy consumption
- Cost

#### 3.5.3.1 Desalination: CDI and competing reverse osmosis (RO):

General:

- Pressure
- Water flux (RO: 10 L/m<sup>2</sup>h)
- Salt rejection
- Selectivity
- Membrane fouling
- Recovery range, feed water recovery (RO: ~40%)
- Feed water quality (total dissolved solids, TDS)
- Treated water quality
- Energy consumption (RO: 3-6kWh/m<sup>3</sup>, lowest 1.6 kWh/m<sup>3</sup>)
- Cost impacts
- Food/water health & safety regulations

CDI

- high ion mobility, high adsorption capacity (which is related to the surface area and pore size) and low electrical resistivity (NaCl adsorption capacity of the currently carbon-based materials is in the range of 0,1–10 mg/g, new materials need to be much better [220])
- The final and ultimate limit to the pore size is the bare ion size. For example 1.16Å for Na and 1.67 Å for Cl. These numbers increase for solvated ions with 3.58Å for sodium and 3.31Å for chloride. Larger pores provide better transport pathways, however, they also decrease the total specific surface area. Besides, the porosity and pore architecture of entire CDI electrodes needs to be considered rather than only the pore characteristics of individual porous particles.

### 3.5.4 Roadmap for filtering, desalination/deionization and membrane applications

#### 3.5.4.1 Current maturity: applied research towards first applications

First graphene containing membranes are investigated for commercial use: Perforene (Lockheed), CNM Technologies

Also GO enhanced polymeric membranes are investigated: G2O

CDI: No reproducible proof of improved effect of graphene available yet, only lab scale CDI tests done

Sensing membranes are still at the lab stage.

### **3.5.4.2 Barriers/Challenges (summarized)**

#### **3.5.4.2.1 Membranes**

- Increased durability
- Selectivity (Functionalization?)
- Prove promising potentials in relevant devices
- Find optimal pore density for optimal stability and permeation (trade off between water flow and mechanical stability)
- Reliable/exact and economically feasible (nano-)pore fabrication
- Scalable manufacturing process
- Compete with Zeolites, CNT, Silica, TiO<sub>2</sub> and silver nanoparticles and thin film composites (TFC)
- H&S regulations: approval for use case
- Sensing capabilities: show improved performance towards competing technologies

#### **3.5.4.2.2 Additional challenges for CDI**

- Performance of CDI compared to state of the art RO
- Design of module and support for graphene
- Scale up to square meter sized electrodes while keeping electrical drive well connected for high homogeneity of current
- H&S regulations: approval for use with drinking water

### **3.5.4.3 Potential actions**

If the area of graphene/2D as/in membranes is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

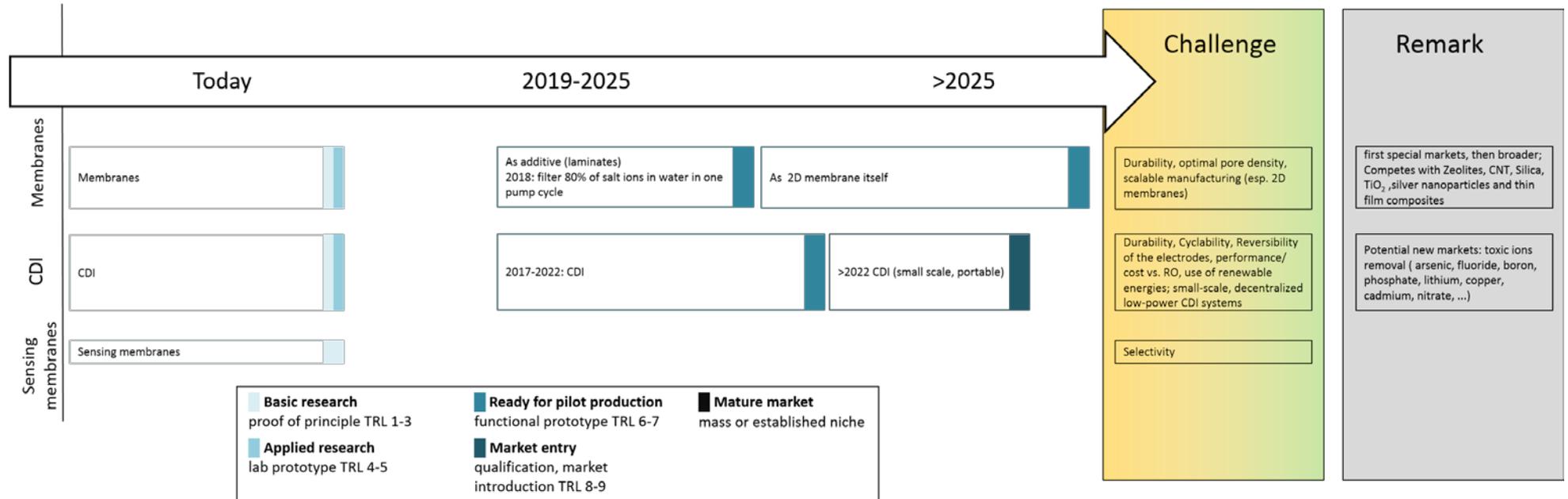
Membranes:

- Experimentally show clear potential and improvement towards SOTA
- Clearly prove performance as close to the application as possible (e.g. in RO configuration)
- Develop scalable manufacturing concepts and compatible form factors
- Address functionalization to improve selectivity
- Address H&S from the earliest developments
- For sensing membranes: address potential concepts for sensing, elaborate clear benefits towards state of the art and competing technologies

## CDI:

- Optimize and scale up electrode preparation
- Optimize contacting of electrode
- Transfer from lab scale to actual demonstrator and prove higher performance compared to activated carbon
- Real life testing to allow assessment of cost-benefit and quality of treated water

### 3.5.4.4 Roadmap



### **3.5.5 Conclusion for filtering, desalination/deionization and membrane applications**

Membranes for filtering, deionization and separation are increasingly important for drinking water and purification of gases or liquids. 2D materials can be used for this component in several ways: as a perforated membrane itself, as an additive or coating to common polymer membranes or as an electrode for capacitive deionization (CDI).

In terms of membranes made from 2D material sheets (perforated), the maturity is still rather low, however the theoretical potential is promising. Due to the new kind of material there are still many questions open, in particular how to approach the trade-off between water flow and mechanical stability, but first commercialisation efforts are taken (Lockheed in USA, CNM technologies in Europe). However, the barrier for implementation is still high due to many open questions. As a layered structure membrane (GO laminates) the implementation is potentially easier, but the cost/benefit is also not yet clear

As an additive or coating to existing membranes, graphene materials are easy to integrate and more mature. The additives shall increase mechanical stability, anti-fouling and water permeation. First commercial activities are also approached (e.g. G2O).

As an electrode for CDI, graphene is a promising candidate. CDI is a promising desalination method with reduced energy consumption. Demonstration of an enhanced performance through the use of graphene materials is pending.

Most importantly, for the use in water purification the environment, health and safety concerns need to be addressed and disproven.

In terms of markets it is expected that the need for purification (of gases or liquids) and for drinking water production will increase. Besides, there are potential integrators in Europe.

Table 21: Assessment of market and technological potential of graphene/2D materials use in membranes and filters on a scale - -, -, 0, +, ++.

Applications	Current technological potential (USP)	Market potential (EU perspective)
Membranes for water filtering/desalination	0	+
Membranes for other filtering	0	+
Membranes with sensing capability	+	0/+
Polymer membrane coating/additive	+	+
CDI electrode	+	+

### 3.6 Special application: (Photo-)catalytic material/enhancement

Functionalized or chemically modified graphene flakes and GO can be also used as catalysts to replace for instance precious metals (see also chapter 4.2). Another specific application area is the use as photocatalytic enhancer for TiO<sub>2</sub>, e.g. for air purification or photocatalytically active self cleaning surfaces [234], for treating contaminants and bacteria [235] and for photocatalytic water cleaning [200]. [199] It is such photocatalytic enhancement for decomposition of contaminants and bacteria and, in general, for cleaning applications that is covered in this chapter.

The enhancement of photocatalysts (and catalysts in general, e.g. for oxygen reduction reaction ORR) can also be used in other applications, such as fuel cells or water splitting. These areas are not covered here and can be found in chapter 4.2.

The general use of 2D materials and their heterostructures as catalysts (also as electrocatalyst and heterogeneous catalyst) is still in its infancy. They have shown considerable potential, but application-orientated research has just started. [236]

#### 3.6.1 Market perspective: graphene/2D as (photo-)catalytic material/enhancement

The global market for photocatalyst products increased from \$1.4 billion in 2013 to nearly \$1.5 billion in 2014. It is estimated to be valued at nearly \$1.6 billion in 2015 further growing at a CAGR of 12.6% until 2020, reaching nearly \$2.9 billion. [237]

To get an idea of the European industrial base, the production value of machinery and apparatus for filtering or purifying gases by catalytic process (excluding intake air filters for internal combustion engines, machinery and apparatus for filtering or purifying air) was 3.6b€, for filtering or purifying air (excluding intake filters for internal combustion engines) was 2.1b€ in 2014. Titanium oxides accounted for a production value of 1.2b€ and preparations based on TiO<sub>2</sub> accounted for 2.3b€ in 2014. [155] These categories do not necessarily resemble the industrial base for photocatalytic functionalities, but at least give an impression of the production values in related areas, where photocatalysts are a subset of.

### **3.6.1.1 Market Opportunities**

#### **3.6.1.1.1 Construction sector as main market for photocatalytic material**

The photocatalyst products are to a large extent used in the construction sector: construction accounts for ~90% of the market. It is projected to grow with a CAGR of 13% from nearly \$1.4 billion in 2015 to \$2.6 billion in 2020. [237]

This growing demand comes from increasing urbanization and the need for reduction of increasing air pollution.

Non-refractory surfacing preparations and protective preparations (fire, water) in the building industry account for a production value of €1.8 billion in 2014 in Europe. [155]

The overall market is rather small at the moment, but there is also not much competition on the market.

In terms of European adopters, the annual total added value of the European cement and concrete industry was €56 billion in 2013. [154] The production value of ready mixed concrete was 16.1b€ in 2014. [155]

#### **3.6.1.1.2 State of the art photocatalytic technologies not feasible at the moment**

There are already coatings/paints and cements on the market that make use of TiO<sub>2</sub> for photocatalytic self-cleaning and air purification. However, the performance is currently not good enough to allow a broad uptake of the technology for the current price tag.

A major disadvantage of the state of the art technology is the need of strong UV light sources, which makes the application not feasible for inside moderate light conditions.

The performance is good enough for outdoor applications where the UV component of the solar radiations satisfies the TiO<sub>2</sub> band gap. Moderate indoor light conditions and

seasonal/diurnal variations of sunlight intensity and clouds, however, create the need for photocatalytically active materials that work with a broad wavelength range and in lower light conditions.

This deficiency creates a need for photocatalytically active materials that work with a broad wavelength range and in lower light conditions. Here, GO could act as an enhancer for the TiO<sub>2</sub> photocatalytic activity.

### 3.6.1.1.3 European strengths in catalysis in general

Europe is an innovative and strong player in catalysis in general, see Figure 47 on the left. This of course also includes catalysts for chemical reactions, fuel cells, exhaust gas cleaning etc. Also in the field of photocatalysis, Europe is strong, see Figure 47 on the right. This field is gaining importance.

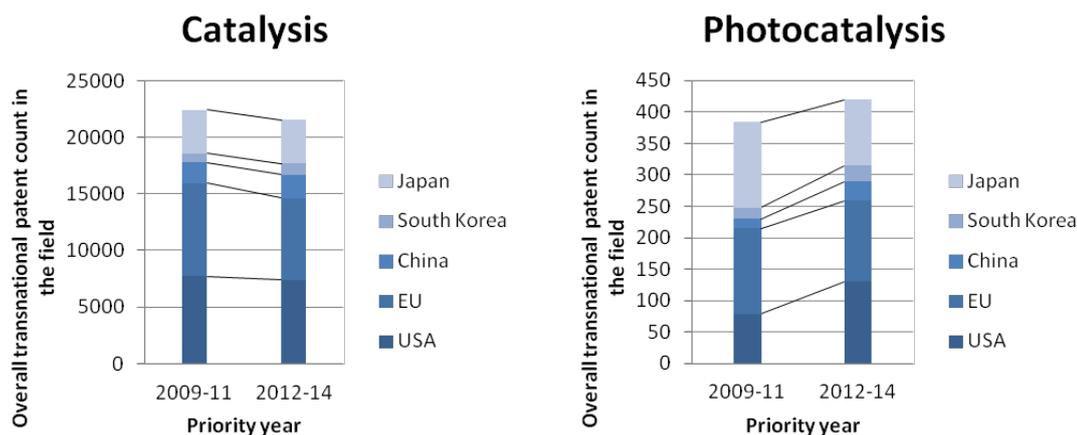


Figure 47: Overall transnational patent count in catalysis and photocatalysis. 2012-2014 values are projected.[137]

At the European Inventor Awards 2014, organized by the European Patent Office (EPO), TX Active, the photocatalytic technology developed by Italcementi, was on the podium at the “Oscar” of innovation.

### 3.6.1.2 Market Threats

#### 3.6.1.2.1 Price sensitive markets with large volumes

An issue for a successful integration of new technologies in this particular market is the very high price sensitivity of construction materials and the large quantity of material needed. Typical coatings/paints cost on the order of 1 €/kg to 3 €/kg on average, even with functionalities, nevertheless market price is much higher, from 15 to 30€/kg. Paving

in photocatalytic blocks costs on average between 10 - 20% more than traditional paving in the materials [238], but only 3-5% adding the cost of manpower. Already this is in parts cost prohibitive in the current market with the current performance.

It appears that the market is not ready for a broad uptake at the moment as the necessity is often not yet seen and the feasibility due to additional costs is not convincing for many decision makers in the buildings industry. There are more or less only lighthouse projects realized with the current technology at the moment. But there is a large potential for the application of this technology to reduce pollution in the cities, provided that their need to be more “green and healthy” is assured by regulations and attention to costs is addressed also at reducing people diseases caused by a polluted environment. A coating a surface area of 1000m<sup>2</sup> with photocatalytic-based products equals eliminating the pollution caused by 30 petro-fueled vehicles or also equals to planting 80 deciduous trees.

#### **3.6.1.2.2 Other emerging technologies under investigation**

There are also other strategies pursued and possible, so that the graphene material solution is currently not so unique. Other strategies are doping or dye sensitization. However these technologies are also not commercially feasible yet. [234]

### **3.6.2 Graphene/2D materials perspective: Current strengths, weaknesses and challenges for the use as photocatalytic material/enhancement**

#### **3.6.2.1 Current strengths of graphene/2D materials use as photocatalytic material/enhancement**

##### **3.6.2.1.1 Proven photocatalytic enhancement of TiO<sub>2</sub> through graphene materials**

Graphene materials enhance the photocatalytic activity of TiO<sub>2</sub>, the latter being used for photocatalytic coatings, e.g. for self cleaning or air cleaning. This is proven for composites of graphene material and TiO<sub>2</sub>.

In order to tackle more efficiently seasonal/diurnal variations of sunlight intensity and clouds negative effects, new TiO<sub>2</sub>-based nanophotocatalysts incorporating graphenic materials have been recently studied and proved to be more effective than titania.

They have better performance under solar radiation and hence are more valid to face variable sunlight intensity over the year and over different latitudes.

The new G-TiO<sub>2</sub> system is expected to be more active under visible light irradiation and to exploit a larger portions of sunlight thereby becoming potentially applicable for indoor cement coatings. Initial experimental results of the research are promising. The TiO<sub>2</sub>-

graphene nanocomposite absorbs light from the whole visible region, the photocatalytic activity of the hybrid material is proven to be enhanced in the visible region. [239, 240] The potential to use visible light will make functionalised cementitious coatings suitable for indoors.

### **3.6.2.1.2 Implementation as a paint or filler**

The application of such a graphene material enhanced  $\text{TiO}_2$  could be done as a paint (see chapter 3.3 for further considerations) or skimcoat. It could be integrated with cement or concrete and coated on large wall areas in cities or streets, also in the form of tiles. Paving of photocatalytic sandwich blocks, with only the upper surface composed of photocatalytic material, is a doable application already on the market for the photocatalysts currently available.

The photocatalytic activity is also influenced by the interaction with the cementitious matrix which is subject to the hydration process and generates new hydrated products (C-S-H, portlandite). It is still open whether this interaction is beneficial or detrimental or has no effect.

The scalability of the processes are not expected to be a major problem.

### **3.6.2.2 Current weaknesses and challenges of graphene/2D materials use as photocatalytic material/enhancement**

#### **3.6.2.2.1 Cost as limiting factor**

The applications dealing with air purification and self cleaning are large area applications and require a rather low cost for broad implementation, e.g. in buildings or pavements. Massive application of photocatalytic cement for walls and pillars is not convenient as the photocatalytic action is present only at the exposed surface. Application of photocatalytic paints or skimcoats is a convenient solution to get cost effective results.

However, already a 150€/kg for the graphene material represents an accessible cost for wider use.  $\text{TiO}_2$  particles are ~20€/kg. The photocatalytic performances of graphene doped  $\text{TiO}_2$  increase also at very low concentration of graphene material. Assuming a 5-10% doping of  $\text{TiO}_2$  with graphene materials, it is possible to improve  $\text{TiO}_2$  particles with 7,5-15€/Kg.

Considering the case of 1kg of coating and a usual  $\text{TiO}_2$  content of less than 5% (50g), a graphene doping of 5-10% of the  $\text{TiO}_2$  content (2,5-5g) implies a formula cost increase of 0.38-0.75€ for a kg of photocatalyst coating. Current formula costs are estimated around 1-3€/kg, not considering production cost and earnings. Assuming a price of 15€/kg for the finished product, a broad gap to put in the formula cost increase due to

the graphene material is available. But development is needed to limit also the applicative cost on the substrate, which might be reached acting on the composition and the technology.

#### **3.6.2.2.2 Necessity of dispersion and unclear performance in final matrix**

In order to have an effective enhancement of the photocatalytic activity, TiO<sub>2</sub> and graphene material need to be in direct proximity and well dispersed in the product. This needs to be achieved in a mass production compatible and simple process. The right functionalization might be a potential solution. The best solution is the preventive preparation of hybrid TiO<sub>2</sub>/graphene material that can be dispersed directly in the cementitious matrix, maintaining the contact between the two compounds.

Besides, as the cementitious matrix evolves over the hydration time, it has to be better investigated how the developed micro/nano structure affects the photocatalytic activity. It is still open to investigation whether the potential interaction is beneficial or detrimental or has no effect.

### **3.6.3 KPIs for photocatalytic material/enhancement**

- Photocatalytic activity (wavelength dependence), under artificial light, under sun light, under diffuse light.
- Price (1 €/kg to 3 €/kg on average for building coatings, 20€/kg for TiO<sub>2</sub>)
- Decomposition of main pollutants (NO<sub>x</sub>, ...)
  - o UNI 11259 standard "Determination of the photocatalytic activity of hydraulic binders. Rhodamine test method"
- Large scale production
- How to apply (painting, spraying, tiles, paves, cement, concrete... should be applicable with common building technologies)

### **3.6.4 Roadmap for photocatalytic material/enhancement**

#### **3.6.4.1 Current maturity: statement**

Many buildings exhibit the current commercial photocatalytic cement (TX Active©-Italce-ment) and NO<sub>x</sub> falls of about 50% were the final proof of the technology (marketed version not containing graphene materials).

Nanocomposites based on graphene material and TiO<sub>2</sub> integrated in a cementitious matrix, were studied with positive results permitting to file a commercial patent and a lab demonstrator was made. Development of new nanocomposites for indoor applications are in progress.

#### **3.6.4.2 Barriers/challenges (summarized)**

The main barriers currently are:

Catalysis in general:

- Fundamental understanding of catalytic nature missing [236]
- Actual integration in a product-like environment (moulding, assembly)
- Testing and feasibility study
- Large scale production of adequate quality (not too good, not too bad) with adequate cost

Photocatalyst:

- Maintaining the performance in the final matrix
- Dispersion of graphene/TiO<sub>2</sub> hybrid photocatalyst in the matrix
- Developing technical paint and/or skimcoat
- Reliability and durability against weather and temperature
- Price
- Market uptake of current photocatalytic technology slow at the moment
- Increasing awareness of policy makers/builders towards the advantages of the photocatalytic technology for “healthier” cities to tackle the slow market uptake of the current technology

### 3.6.4.3 Potential actions

If the area of graphene/2D as photocatalytic material/enhancement is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

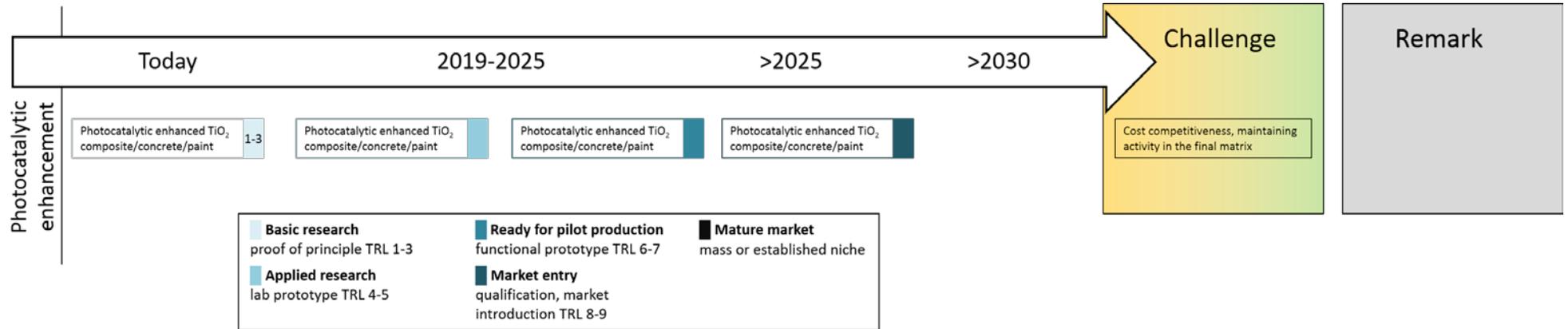
Basic understanding:

- investigate the catalytic nature of these materials by means of in situ characterizations and theoretical simulations [236]
- Understand the underlying physics to better tune the properties

Engineering actions:

- Investigate preparation technologies to meet adequate quality, scale and cost
- find best host(s), assemblies or moulds
- Testing under relevant conditions
- Assess commercial viability
- improve dispersion with TiO<sub>2</sub> (photocatalysis specifically)
- investigate integration into host/matrix material(photocatalysis specifically)
- Develop standards for testing photocatalytic performance

### 3.6.4.4 Roadmap



### 3.6.5 Conclusion for photocatalytic material/enhancement

The photocatalytic activity of TiO<sub>2</sub> is enhanced in the presence of graphene material. This is an interesting and rather simple application for photocatalytic paints or coatings for air purification and self-cleaning surfaces. The market is currently not very large but expected to grow. In particular, the greater and greater demand for healthier cities is favorable for the application of the technology. As a drawback the cost seems to be a limiting factor since the construction sector has difficulties to charge it on the customer. The advantages for the urban environment should be better disclosed. It seems likely that the policy makers are not enough sensitized to the technology. Importantly, the competition is not very strong at the moment.

However, the dispersion of the graphene material in the host needs to be better understood to come to a commercially viable process. The actual performance improvement of the material mix of TiO<sub>2</sub> and graphene material also needs to be proven on relevant scale and conditions. The price sensitivity of the potential application as a large scale paint/skimcoat can act as a barrier, which requires low cost base materials to be passed. Nevertheless, the low thickness of the coating, 2-3mm, permits to limit the formulation cost and development is needed to limit also the applicative cost on the substrate.

Table 22: Assessment of market and technological potential of graphene/2D materials use for photocatalytic material/enhancement on a scale - - , -, 0, +, ++.

	Current technological potential (USP)	Market potential (EU perspective)
photocatalytic enhancement	++	+

### 3.7 Summary composites and bulk applications

The application area of composites and coatings is the area which is closest to application (or already there). However, the products on the market address niches, where a new technology can be used for advertisement, such as in sports equipment.

For broader markets, the cost/benefit of graphene/2D materials use is often not clear enough, although companies are more and more interested to investigate the actual potential. A very important issue is that the expectations need to be managed (“100x stronger than steel”), which will never be reached in a composite. For bulk applications and mass markets, often cost and performance need to be improved.

Important assets are functionalisation, biocompatibility/recycling and multi-functionality.

In general, the applications where graphene/2D flakes are used, such as in composites, paints, liquids, have a lower implementation barrier and markets can be easier addressed, compared to e.g. electronics. On the other hand, the technological added value (performance improvement and disruptiveness) is probably smaller for flake based bulk applications compared to high quality films. Coatings or membranes made from high quality (single layer) films will probably only reach markets with rather small surface areas, (e.g. TCFs). The implementation barrier is currently too high. This type of coating can benefit from wafer scale integration in electronics.

Table 23: Summarized assessment table of all composites and coatings application areas primarily sorted by European market potential and secondary sorted by USP.

<b>Composite property/host</b>	<b>Current technological potential (USP)</b>	<b>Market potential (EU perspective)</b>
<b>Composites: Multifunctional enhancement; added functionalities</b>	++	++
<b>Multifunctional coatings (added functionality)</b>	++	++
<b>Composites: Thermal enhancement (polymers, ceramics)</b>	+	++
<b>Composites: Electrical enhancement (polymers, ceramics)</b>	+	++
<b>Composites: Barrier (polymers)</b>	+	++
<b>Composites: Polymers</b>	+	++
<b>Barrier coatings (anti-...)</b>	+	++
<b>Composites: Mechanical enhancement</b>	+	++
<b>Composites: Ceramics</b>	+	++
<b>photocatalytic enhancement</b>	++	+

<b>Composite property/host</b>	<b>Current technological potential (USP)</b>	<b>Market potential (EU perspective)</b>
<b>Polymer membrane coating/additive</b>	+	+
<b>CDI electrode</b>	+	+
<b>Electrical coatings</b>	0/+	+
<b>Composites: Flame retardant (polymers)</b>	0	+
<b>Composites: Metals</b>	0	+
<b>Composites: Cement/concrete</b>	0	+
<b>Thermal coatings</b>	0	+
<b>Membranes for other filtering</b>	0	+
<b>Membranes for water filtering/desalination</b>	0	+
<b>Lubricants (wet)</b>	0	+
<b>Membranes with sensing capability</b>	+	0/+
<b>Adsorbent for remediation</b>	0	0
<b>Transparent conductive films</b>	0	-
<b>Drilling Fluids</b>	0	-