ADOPTING MULTIFUNCTIONAL MATERIAL SYSTEMS

by

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A Dissertation Presented to the

Faculty of Engineering

of the

University of Oporto

In partial fulfillment of the requirements for the Degree of

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

OPORTO, JULY 2015

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ABSTRACT

ADOPTING MULTIFUNCTIONAL MATERIAL SYSTEMS

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July 2015, 174 pages

An increase in system-level efficiency and polyvalence of products and components is one of the main advantages of the use of some novel polyvalent materials and structures. This polyvalence or multifunctionality is currently a hot topic in science and engineering circles and is gathering increasingly more attention. Presently this multifunctionality can be achieved by stimuli responsive materials such as temperature, stress and light, by using shape memory materials, by using surface structures with anti-biofouling and drag reduction capabilities, among many others. In this dissertation, an overview is presented of the topic, including state-of-the-art review, challenges, suggestions and proposed methods to overcome them and to increase innovation in developing both these materials and structures and the products that contain them.

Keywords: multifunctional composites; multifunctional structures; multifunctional materials; material innovation; product innovation.

RESUMO

ADOTANDO SISTEMAS DE MATERIAIS MULTIFUNCTIONAIS

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Mestrado Integrado Engenharia Mecânica

Orientador: Prof. Dr. A.T. Marques

Julho de 2015, 174 páginas

Um aumento da eficiência total dos sistemas e a polivalência de produtos e componentes é uma das principais vantagens do uso dos novos materiais e estruturas com funcionalidades múltiplas. Esta polivalência ou multifuncionalidade está cada vez mais a ganhar mais atenção nos círculos científicos e de engenharia em todo o mundo. Atualmente esta multifuncionalidade pode ser conseguida pelo uso de materiais sensíveis a estímulos, tais como temperatura, tensão e luz, pelo uso de materiais com memória de forma, pelo uso de estruturas superficiais com capacidades antibacterianas e de redução de arrasto, entre muitos outros. Nesta dissertação é apresentada uma visão geral do tópico, incluindo o estado da arte, desafios a vencer, sugestões e métodos para os ultrapassar e para aumentar a inovação na criação de novos materiais ou estruturas multifuncionais e produtos que os contenham.

Palavras-chave: compósitos multifuncionais; estruturas multifuncionais; materiais multifuncionais; inovação de materiais; inovação de produtos.

ACKNOWLEDGEMENTS

To Dr. António Torres Marques, supervisor of this thesis, I thank very much for the support given throughout the elaboration of this dissertation. I had the good fortune of having a supervisor with whom I share similar futuristic visions.

To Dr. António Augusto Fernandes and Dr. António Barbedo de Magalhães as two great Portuguese teachers and engineers whose focus on innovation and out of the box thinking have also been a personal inspiration.

To Elon Musk for being an inspirational engineer, for showing the world – in a few years the reader will fully understand – what it's like to do good for the sake of humanity and not just for the sake of one-self.

To my dear family and dear friends who understood and sometimes endured my dedication to learning.

To the many scientists and engineers whose work I got the opportunity to take knowledge of and, from which I understood, also have a great driving passion to improve our world.

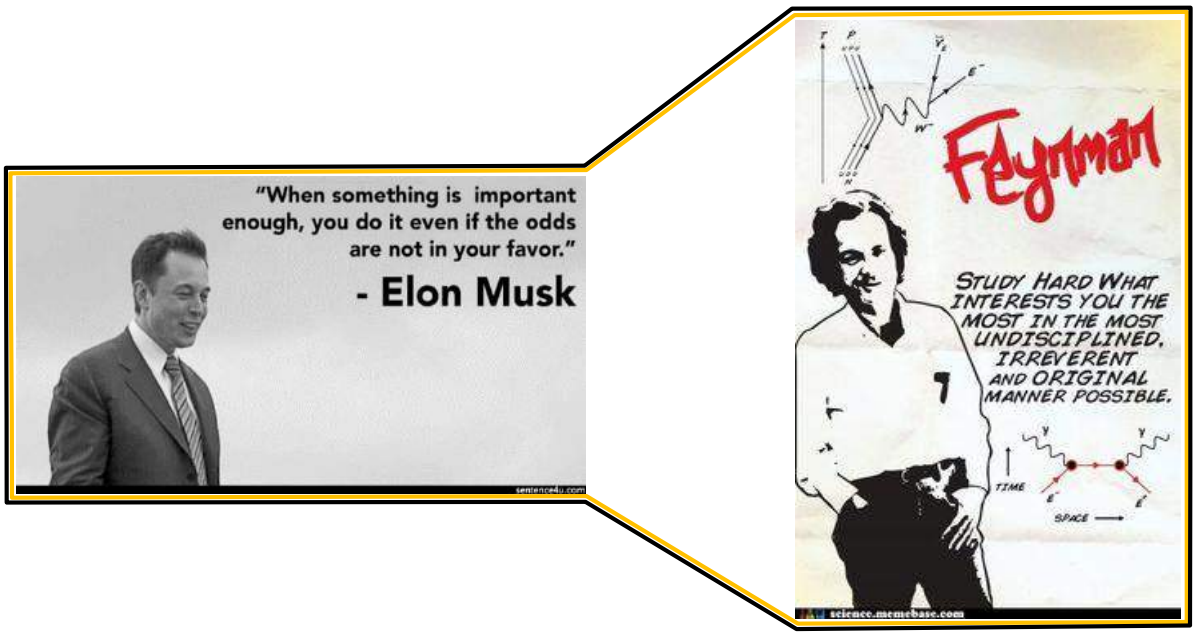

"When something is important enough, you do it even if the odds are not in your favor."
- Elon Musk
Feynman
STUDY HARD WHAT INTERESTS YOU THE MOST IN THE MOST UNDISCIPLINED, IRREVERENT AND ORIGINAL MANNER POSSIBLE.
TIME
SPACE

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LIST OF SYMBOLS AND ABBREVIATIONS

AI	Artificial Intelligence
AFC	Active fiber composite
CF	Carbon fiber
CNT	Carbon nanotube
CNF	Carbon nanofiber
CVD	Chemical vapor deposition
E	Young's modulus
FGM	Functionally graded materials
FEA	Finite element analysis
GF	Glass fiber
IR	Infrared
MFS	Multifunctional structures
MFC	Multifunctional composites
MFC	Macro fiber composites
MFMS	Multifunctional material systems
MS	Material systems
MWCNT	Multi-walled carbon nanotube
RF	Radio frequency
SHM	Structural health monitoring
SMA	Shape memory alloys
SMC	Shape memory ceramics
SME	Shape memory effect
SMM	Shape memory materials
SMP	Shape memory polymers
SRM	Stimulus responsive materials
SWCNT	Single-walled carbon nanotube
UAV	Unmanned air vehicles
UV	Ultra violet

Chapter 1 Introduction

1.1 Motivation

Humans are great at taking lumps of stuff and making them useful. This ability to design and engineer products from the basic materials around us is one of the things that has enabled our civilization to become what it is. We have been incredibly successful in adding value to the material we mine, grow or collect.

If we roughly plot the discovery of materials against time (**Fig. 1**), we get a graph in accordance to the law of accelerating returns proposed by Kurzweil according to which the rate of change of the growth of technologies tens to increase exponentially [1, 2].

The stone, bronze and iron ages are periods belonging to the three age system of archaeology, which takes into account the most prominent materials at each stage. After the long Stone Age, copper is credited as the first metal ever used by humans. Bronze came soon after and really impacted the world at that time, being a landmark in human achievement. Since then, man has been experimenting with one form of alloy or the other with the sole reason of improving their properties. Then polymers started gradually appearing and with them advanced composites. After the first three ages, no material has yet been given the honor of being the current most important, but one could argue it is silicon. Another aspect we can observe is that for the longest time in our history, the vast majority of materials have had only one function, and that's structural. As time progressed, as new materials were discovered and human knowledge increased, materials started performing new functions, such as thermal resistance and conducting electricity, sometimes simultaneously. We're now very close to another phase, as new revolutionary are discovered, such as carbon-based nanocomposites, and our ability to tailor the existing ones, especially at the small size scales, improve. If we are to approach ideality, and that's the path technology seems to be headed because that's where it has been moving towards to [3], it is to expect that all materials and structures perform several functions, meaning that in the future most, if not all, materials and structures will be multifunctional.

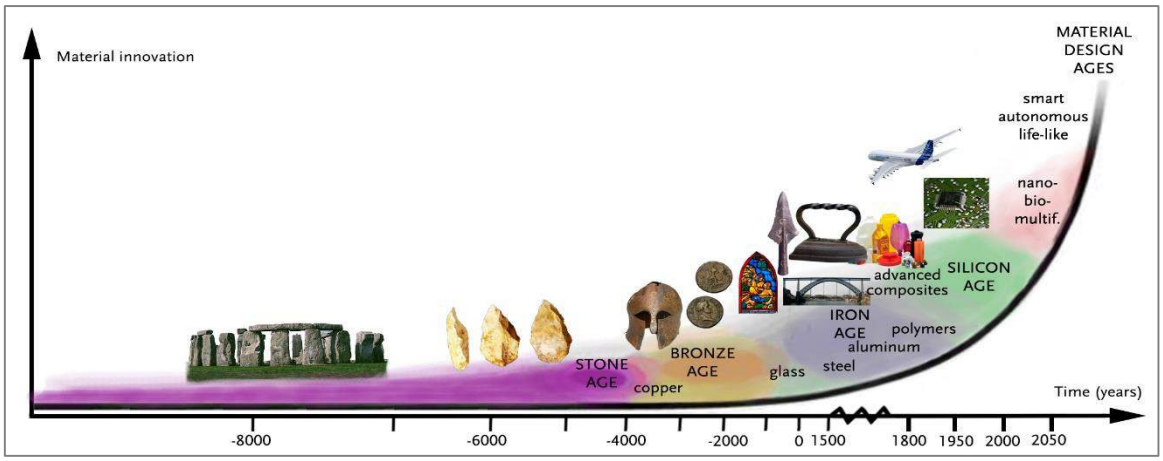


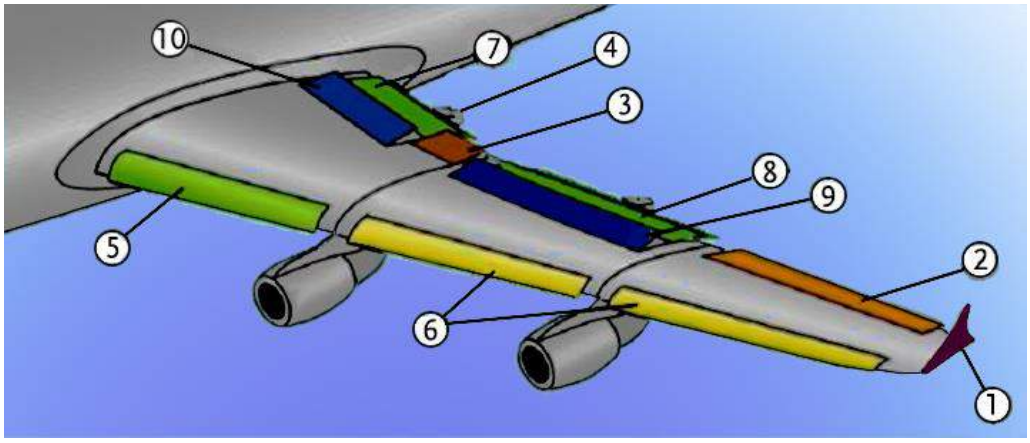
Fig. 1 – A material-based age classification according to the law of accelerating returns. Based on [4]. Images from [5-15] .

Materials that have as their main function to bear loads are denominated "structural materials" and they generally have a few good mechanical properties such as high strength, stiffness, fatigue resistance, fracture toughness, ductility, damping, tenacity and thermal stability. There is a tendency in some engineering fields to give more importance to the structural functional but I am of the opinion that other functions are just as important and as the time passes may tend to be even more so. The semiconducting ability of silicon is such an example. For this reason, in this dissertation, all functions will be given equal importance.

In **Fig. 2** a schematic of the exterior of an airplane wing is presented and the description of the function of each part. We can see that currently these wings have several independent parts each for a different function. Each of these separate parts require independent electrical wiring, actuators and structural materials. The problem with this is an increased drag and weight which reduce flight endurance time and increase complexity, which increases cost and time to design and manufacture.

When metals are used, lots of small parts are preferred. One of the reasons is that in large parts it's harder to predict crack propagation. Co-bond is when you have two already cured parts and you want to cure those two parts together (into one). So, in composites you can co-cure or co-bond a structure reducing the number of parts.

Nevertheless, the fact that we're using different parts to perform different functions is very inefficient because each of those parts is not good at anything other than its function. Now, the wings are just one part of one of the subsystems of the airplane (**Fig. 3**). For example, the wires needed to conduct electricity for the actuators, apart from conducting electricity are a dead weight for the aircraft costing tons of CO_2 per year to the atmosphere for the excess of fuel needed to move them.



1 – Winglet: keeps high pressure air under the wing from spilling over the wingtip and robbing the tip of the lift or creating drag and vortices	5 – Kruger flap: hinged leading edge flap increases lift while slow, stowed while fast to reduce drag
2 – Low speed aileron: wider for increased lift; placed at wingtip for better control at slower speeds	6 – Slats: sliding leading edge flap increases lift while slow, stowed while fast to reduce drag
3 – High speed aileron: narrow for reduced drag; placed closer to fuselage to reduce overcontrol at higher speeds	7 and 8 – Three slotted flaps: increase lift at slower speeds; increase stall speed; slotted configuration allows more surface area to be deployed
4 – Flap track fairing: houses the flap extension mechanism since flaps separate from wing edge as they deploy	9 and 10 – Spoilers: disrupt airflow over the top of the wing to dump lift; also provide drag for airbraking.

Fig. 2 – An aircraft wing is today constituted by several movable independent parts which increases complexity, weight, and cost. Adapted from [16].

If we are to move to more efficient systems, one requirement is then the use of multifunctional materials and structures. As we will see, we are now in another turning point in materials science – the discoveries of novel materials, the exponential increase in computation power, as well as the discoveries of the functioning principles of biological systems susceptible of biomimetics as well as the unprecedented good means of sharing knowledge are the greatest contributors to this change.

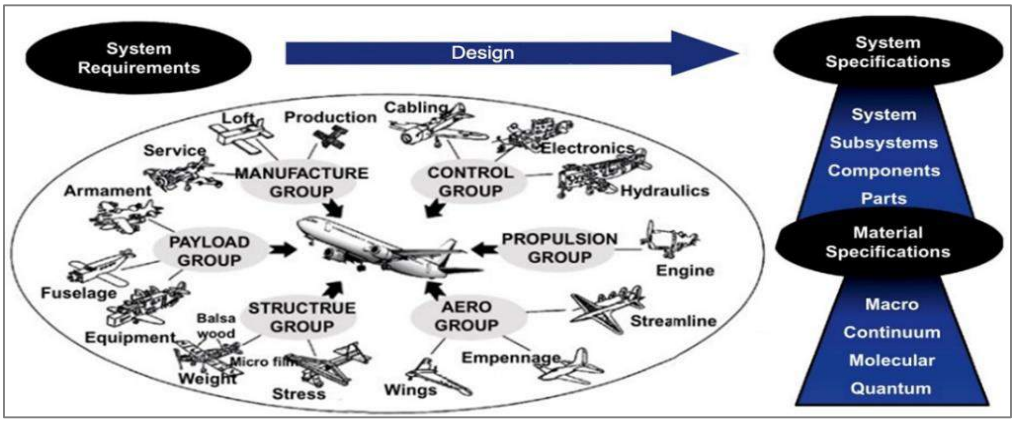


Fig. 3 – Example of the aircraft hierarchical subsystems. Adapted from [17].

1.2 Objectives

This work has as its main goals:

- To identify and define multifunctional material systems;
- To write a state of the art review of current multifunctional material systems;
- To present current challenges in adopting and developing multifunctional materials systems;
- To propose methodologies as a tool to develop innovative ideas for a faster and better development of healthier, safer, more cost effective and more environmental friendly products.

1.3 Structure of this dissertation

Chapter 2 presents definitions of multifunctional material systems and their state-of-the-art. The chapter is introduced with the clarification of what constitutes such a system and then proceeds by clarifying many concepts that are related. The rest of the chapter presents the state-of-the-art.

In chapter 3 the main challenges to overcome are presented namely related to manufacturing and the development of these materials systems.

Chapter 4 concerns proposed methodologies to solve some of those challenges namely creative thinking techniques, taking inspiration from nature, evaluation of performance of multifunctional material systems and increasing sustainability. It is wrapped up by an example showcasing the integration chapter's topics.

In chapter 5 a few provocative ideas are presented where multifunctional material systems could be used and chapter 6 summarizes and exposes the main conclusions to take from this dissertation.

CHAPTER 2

An Overview of Multifunctional Material Systems

2.1 Introduction

In order to adequately convey information, it is essential that the writer conveniently removes ambiguity from the terms used. This is particularly important in a newly developing field such as this of multifunctionality in material science and engineering, where many terms are loosely defined, and some concepts don't even have a term to describe it. Then I would like to make some clarifications I feel are necessary to remove that ambiguity.

Multifunctional materials (MFM), Multifunctional composites (MFC) and multifunctional structures (MFS), which I will group into the broader group of **multifunctional material systems (MFMS),** are those which can perform multiple functions that is, that are polyvalent.

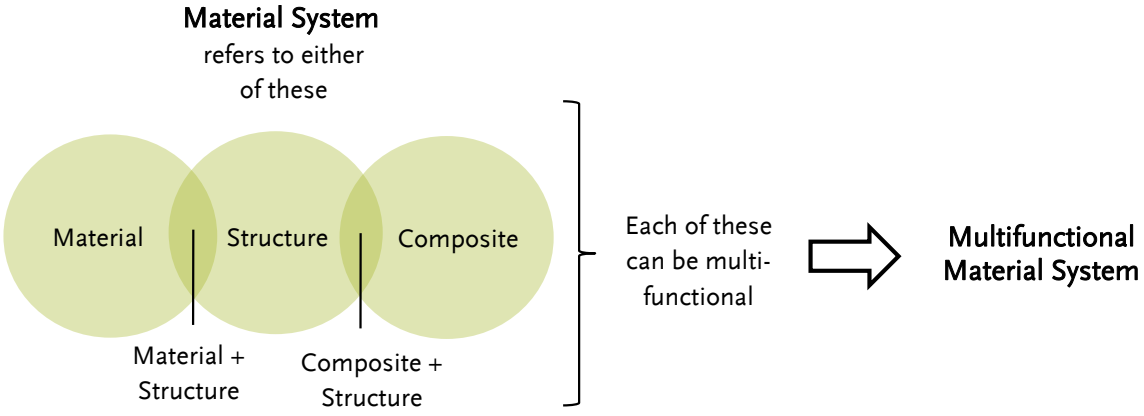


Fig. 4 – Basic nomenclature explanation.

The definition of **material systems** (MS) in this context encompasses materials, composites and structures (**Fig. 4**). The necessity for this definition arose because we could have for example a unifunctional ceramic with a textured surface and an internal structure of a nanolattice. It wouldn't be correct to call it a MFM because the multifunctionality arises

both from the material and the structure. An example of a MFM would be CNTs which inherently have high mechanical strength and electrical conductivity or PZT which can provide both sensing and actuation. An example of a MFC would be epoxy/CF+(Fe powder) (mechanical strength and electrical conductivity), and an example of a MFS would be shark denticles (providing anti-bioufouling and reducing drag). The definition of MFMS, then, encompasses all of these.

Another clarification to make is defining exactly what constitutes multifunctionality. Some authors consider materials with multiple structural functions (e.g. damping and toughness) to be multifunctional, and dividing the functions in two groups: structural and non-structural [18, 19] while others treat structural functions like any other [20]. I see no reason why structural functions should be treated differently. Otherwise one might also divide functions as electrical and non-electrical, or biological and non-biological since there are also a lot of electrical and biological functions. So in favoring of equality, structural functions such as stiffness, strength, ductility and fatigue resistance, here will be grouped as one function.

Some more clarifications will be done, but they will be introduced later on, as first it seems more important to discuss some of the properties and advantages of these MFMS over unifunctional MS which is the basis for studying them in the first place.

MFMS approach the concept of ideality by being more autonomous and polyvalent than their counterpart unifunctionals. Whereas traditionally monofunctional materials and structures have been used in separated parts to perform separated tasks, MFMS allow a single part to serve several purposes, some of those eliminating the need of an external resource, as we would imagine an ideal material would be. An electrically conductive material eliminates the need for wires, a shape morphing eliminates the need for actuators, a flame retardant material eliminates the need for severe fire protection mechanisms, a renewable material minimizes the need for continuing of extraction of raw materials, and of course a combination of these eliminates the need for all of those and maybe some more, because often times the combination of materials can result in new functions not present in either of the single materials by themselves.

The use of MFMS will, and in some cases already do, allow savings in number of parts, reducing the need for joining operations. An effective integration should be able to eliminate traditional boards, connectors, bulky cables yielding major weight and volume savings (**Fig. 5**) increasing system-level efficiency. They should also be vastly more tailorable to the application than current unifunctional materials, because of the wide range of combinations of materials and resulting properties and functions (**Table 1**).

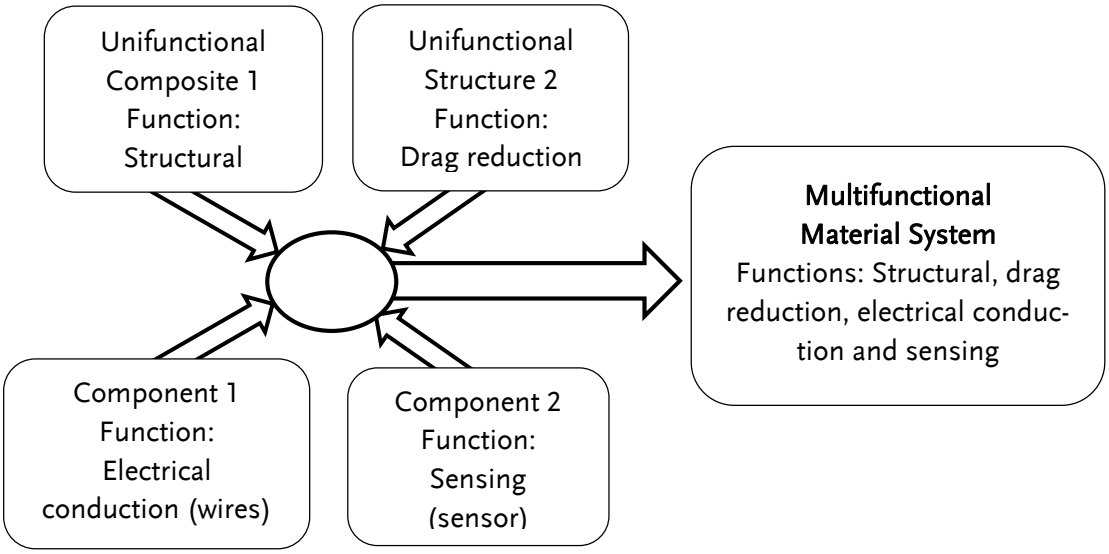


Fig. 5 – A multifunctional material system should integrate in itself the functions of two or more different components and/or composites/materials/structures increasing the total system's efficiency.

Table 1 – Comparison of tailorability and optimization of different types of materials

	Functionally Graded Materials, Nanocomposites, Multiscale and Hierarchical Composites	*Traditional Composites*	*Traditional etals, Polymers and Ceramics*
Tailorability of the material properties	Changing wt. or v/v %, type, size, orientation with or without grading of filler/matrix. Design at the molecular level.	Changing wt. or v/v % and type of filler/matrix	Alloying, thermal treatments
Optimization of parts	Through grading, stacking orders, ply angle, geometry, material and structure combination, hierarchy, surface utilization	Through stacking orders, ply angle and geometry	Through geometry
Ease of adding multifunctionality	Easier ←		→ Harder

An example of the potential advantages of the use of MFMS can be, seen for example, in electric-propelled unmanned air vehicles (UAVs).

The equation below [21] shows that a decrease in the weight of the aircraft increases by 1.5 times the flight time whereas an increase in battery capacity only increases the same variable by a factor of 1. This supports the notion of combining battery with structural parts in order to increase flight time.

$$\frac{\Delta t_E}{t_E} = \frac{\Delta(E_B \eta_B)}{E_B \eta_B} - \frac{3}{2}\frac{(\Delta W_S + \Delta W_B)}{W_{total}}$$

t_E= flight endurance time
E_B= nominal stored battery energy

η_B = efficiency factor of the battery that accounts for the influence of the current draw rate, temperature, etc., on the amount of energy that can be extracted from the battery
W_S = weight of the aircraft structure
W_B = weight of the battery

Besides system performance, the reduction in costs, at least in the post-production phase, that these composites could bring are also something to think about (**Fig. 6**).

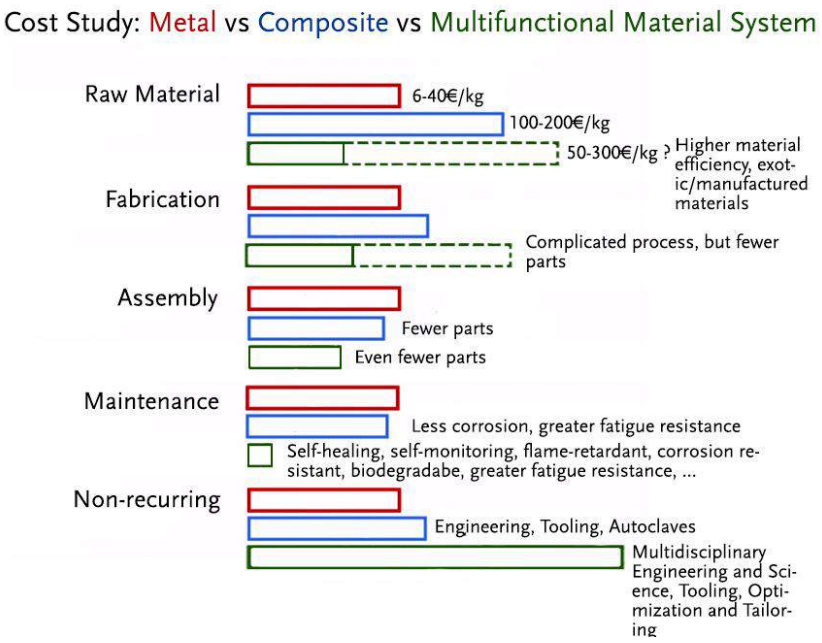


Fig. 6 – Cost study: Metal vs Composite vs Multifunctional Composite.

Below is a detailed explanation for each component of the above figure.

- Raw material:
  - It is to be expected that in most cases different materials will be used in a MFMS, because that's easier than to find a MFM that performs all the desired functions. On the other hand, there are several hierarchical MS being developed, as we will see, that increase material efficiency, thus using less material to achieve a greater performance. It is then unclear where would MFMSs stand in terms of raw material costs. Some may be cheaper others may be more expensive than current materials, but either way, for the same price it is expected that the performance for each function will increase, so the value will tend to get better.
- Fabrication:
  - Currently manufacturing is one the greatest challenges in the production of MFMS, and many methods used are expensive and haven't been transferred to industry because of scalability problems. It is to be expected that these issues eventually subside, but still, since MFMS are of higher complexity than unifunctional ones, it might be the case that their production

will also be more expensive and require more expensive tooling. On the other hand, with the increasingly improving 3D-printing technology some of those difficulties may significantly reduce.

- Assembly:
  - Assembly should be a clear winner for MFMS. Shape morphing technologies and multifunctionality reduce the number of articulated and external components, which in turn reduce the number of parts and therefore joining complexity. For example, if one part made of a MFMS can do functions that used to need 5 different materials/parts, then it's a 5 fold decrease in joining operations.
- Maintenance:
  - Maintenance is the component where MFMS should shine the most. Because of their increasingly autonomous status, self-healing/sensing/regulating (homeostasis)/etc., the need for human control should gradually decrease, and therefore so should maintenance costs.
- Non-recurring:
  - The fact that MFMS require an extensive knowledge often from a wide range of fields, has to have some impact in the final cost of the material. The design phase needs to integrate engineers from several fields as the material itself will satisfy the requirements of several functions of different schools: electrical, mechanical, biological, environmental, chemical, etc. Simulation software, and material databases should get more complex because of this reason.

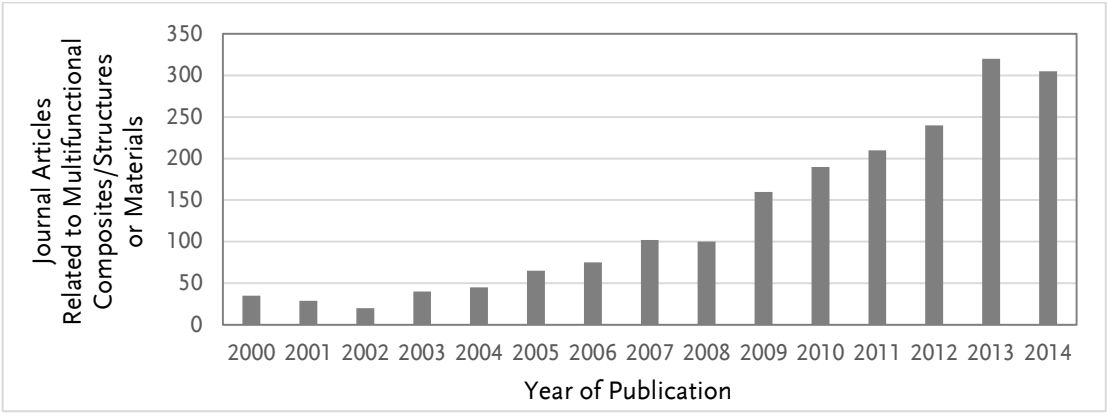


Fig. 7 – Literature survey on journal articles related to multifunctional composites/structures/materials in Engineering Village, March 2015.

The promise that these advantages hold have gradually and increasingly come to the attention of the scientific community, as we can see on a literature survey conducted this years' March (**Fig. 7**).

As the number of people working in a field increases so does the need for clarification. By reading several articles and reviews it quickly becomes clear that many terms are

used interchangeably with slightly different meanings. For example, the term "smart material" is a very lose term whose meaning varies significantly from author to author. I believe that as time goes on, and as these MSs gain mainstream acceptance, there will be need for a defined nomenclature to develop. Hereby I present a few suggestions that might be useful.

Schlaich [22] suggested a nomenclature to characterize the level of autonomy of a system which I find useful and practical (**Table 2**) and perhaps should be used has the way to address the topic of material/system autonomy.

Table 2 – Levels of autonomy of a system [22].

System	Sensor	Actuator	Control	Processor	Power generation and Storage
Passive					
Sensory	●				
Active	●	●			
Adaptive	●	●	●		
Intelligent	●	●	●	●	
Autonomous	●	●	●	●	●

Then there is the scale issue. Nanoscale, microscale, nanomaterials, nanocomposites, are relatively loose terms. For instance, the term 'nanocomposite' is generally applied for composites that have a filler that has at least one of its dimensions in the nanoscale. But then how do we define nanoscale? Many authors define nanoscale as the size from 1-100nm. However, I think a more congruent definition would be more in line with the SI prefixes, that is, nanoscale being 1-1000nm, microscale from 1-1000μm, and so on, otherwise on what scale does the size of 400nm belong to, for instance? Then if more specificity is needed the adjectives 'low' and 'high' might be used as in 'low nanoscale' for 1-100nm and 'high nanoscale' for 100-1000nm (**Fig. 8**).

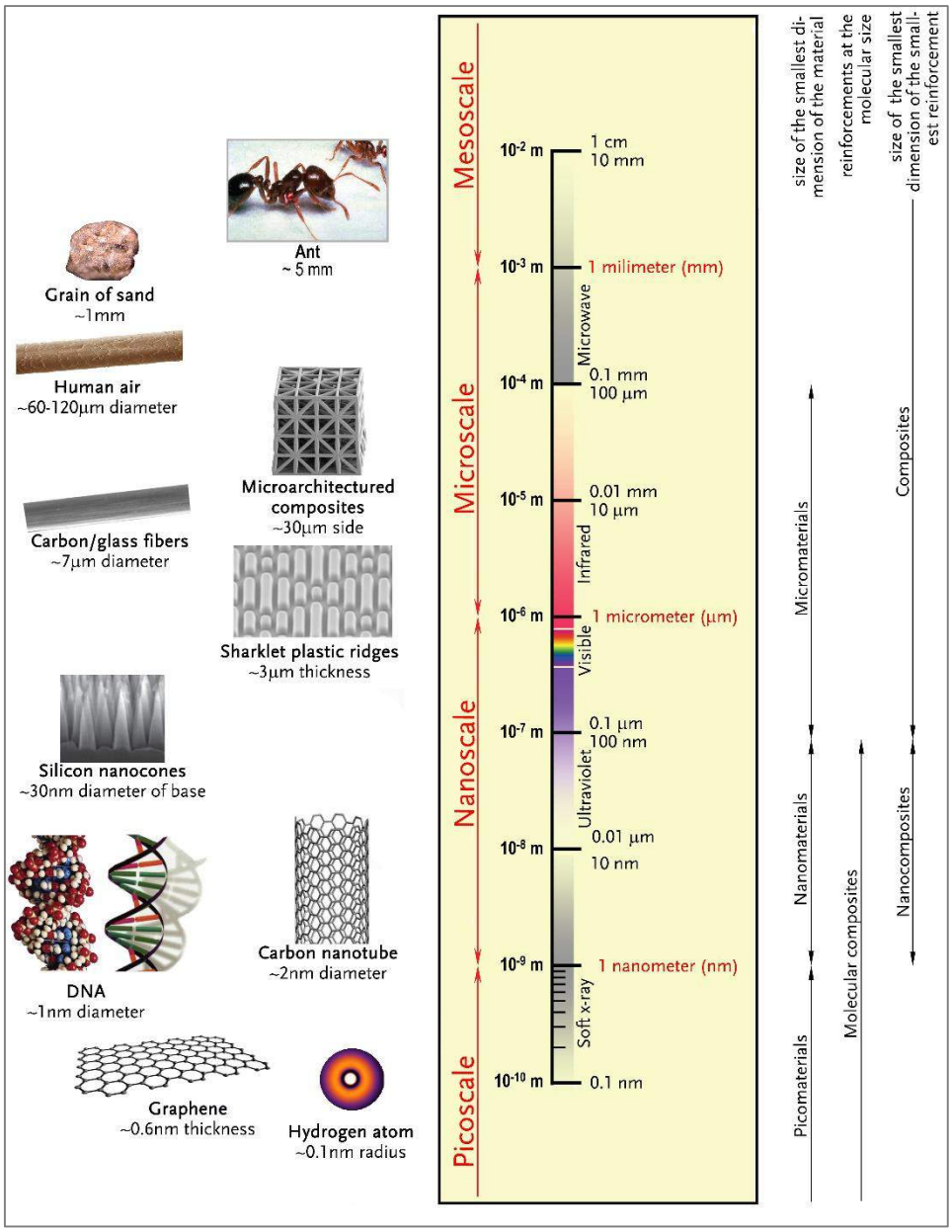


Fig. 8 – A visual representation of materials and structures at different sizes and a proposed classification of materials at different scale levels. Based on Scale of Things [23]. Inset images from [24–31].

Molecular, **nanocomposites** and **composites**, are those in which the reinforcement is realized on molecular level [32], nanoscale (e.g. carbon nanotubes (CNT) reinforced matrix) or micro to mesoscale respectively (e.g. carbon fiber (CF) reinforced matrix).

Pico-, **Nano-** and **micromaterials** are those that exist in a shape that has one of its dimensions in the pico-, nano- or microscale respectively. For example, graphene (picomaterial), CNTs, nanorods, nanoparticles (nanomaterials) carbon and glass fibers (micromaterials).

Other concepts that are going to be mentioned quite a frequently are 'multiscale' and 'hierarchical' composites (**Fig. 9**). Multiscale composites concerns the different sizes of

the fillers. For example, a carbon fiber (micromaterial) + carbon nanotube (nanomaterial) reinforced epoxy matrix is a multiscale composite. A hierarchical composite concerns the structural organization of the fillers, where fillers/materials are organized in a hierarchical way. For example, filler A is contained inside filler/material B, which is contained inside filler/material C. This topic will be further developed in the chapter 'Nature as a source of inspiration'.

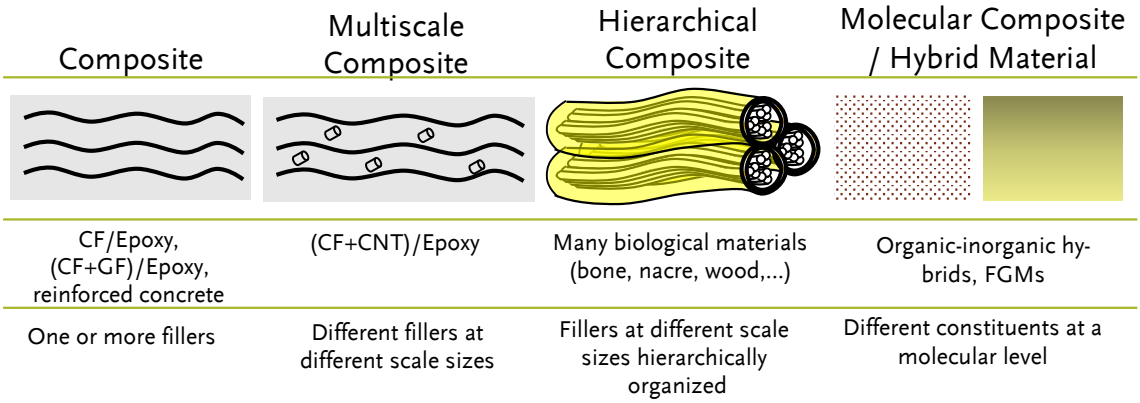


Fig. 9 – Classification of multi-materials according to the types, sizes and organizations of constituents.

Another useful concept for distinguishing material systems is that of material integration, that is, how well materials are integrated into one another. We can obtain multifunctionality by integrating various functions in multimaterial systems or single materials. In the former, it can be obtained by the addition of fillers at the nano or microscale such as in (nano-)composites, or multilayer constructs. For single materials it can be obtained at the molecular level such as with several functionalized polymers.

For now, that we are in the infancy of these materials, 3 levels seem to be enough to differentiate the majority of MFMS, but I would expect a more refined subdivision to occur as the technology progresses and the need for a finer characterization arises.

Matic [33] and Asp et al. [34] have proposed slightly different versions of the same division, a three scale system (**Fig. 10**). The integration of materials goes from not integrated (type I or structure) to integrated but with distinct phases (composite) to fully integrated at the molecular level or type III.

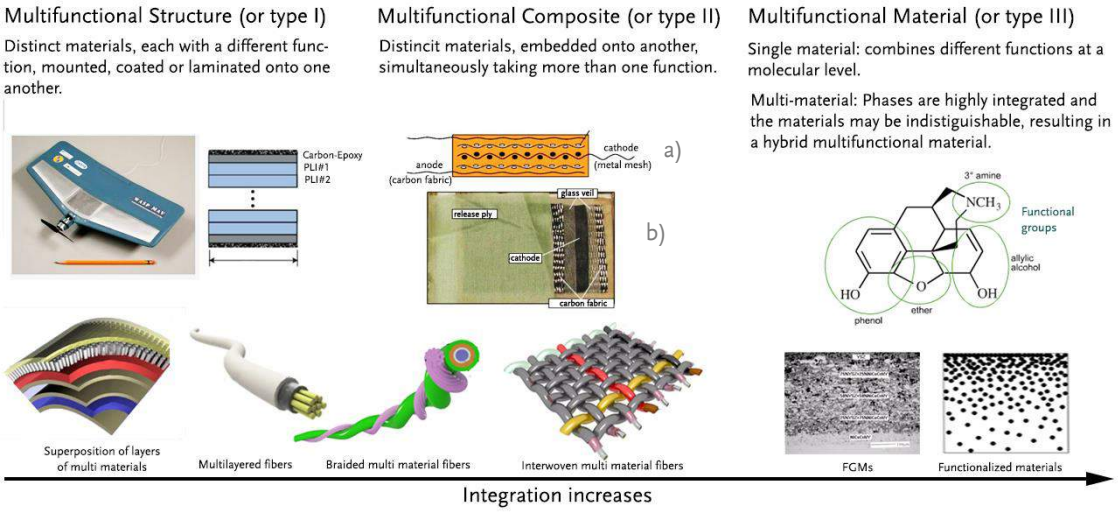


Fig. 10 – Classification of MFMS according to the distinguishing of the constituents: Multifunctional structure, multifunctional composite and multifunctional Material. Images a) and b) from [35, 36]. Scheme based on [33, 34]; Sources of the images used to create this graphic and not presented here are on their respective chapters.

Because we are moving towards smaller and smaller devices that can increasingly easily be embedded inside materials there is another distinction I find useful to make. The difference between a material with an embedded device and a composite. I would argue that for a composite to be called as such, it needs to be homogeneous in at least one direction.

Let's say we need a wall to have sensing abilities, for example to collect vibration data, and we also have a bulky device that can do it. If we put the device outside, attached to the wall can we say the material has sensing abilities or that it's MF? I wouldn't say so. And if we put it inside the wall? Same answer. What if we put it inside and give it the shape of a quadrangular thin film that extends to the whole size of the wall? Yes, it could be called a type I MFMS.

Finally, another interesting concept is that of functional density, which simply means nº functions / volume or mass. As we will see later, currently we're at a point where surface material systems tend to have higher functional density.

2.2 Types of Multifunctional Materials

An important group of materials that are often studied for integration/embedding with others to create MFMS are **stimulus-responsive materials (SRMs)**. These materials respond to a certain stimulus by altering some of their physical and/or chemical properties. Next the prefixes to '-responsive' are presented and the corresponding stimulus to which they are sensitive;

1. **Heat => thermo-**
   - Thermochromic: change color, belong to the chromogenic group;

- Thermoelectric: are able to convert temperature differences into voltage and vice-versa;
- Other thermo-responsive materials: shape memory alloys/polymers/ceramics;

2. **Stress/pressure => mechano-**
   - Smart gels;
   - Piezoelectric: produce a voltage when stressed and change shape/produce stress when they are applied a voltage;
3. **Electrical current/voltage => electro-**
   - Electrochromic: change color, belong to the chromogenic group;
   - Dielectric elastomers: produce large (up to 300%) strains under the influence of an external electric field;
   - Electro-rheological fluids: instantly change shape when applied an electric charge;
   - Electrostrictive: exhibit high electrostriction, that is, they change their shape under the application of an electric field;
   - Electro-active polymers: exhibit a change in shape when subjected to an electric stimulus;
   - Piezoelectric: produce a voltage when stressed and change shape/produce stress when they are applied a voltage;
   - Thermoelectric: are able to convert temperature differences into voltage and vice-versa;
4. **Magnetic field => magneto-**
   - Magnetorheological fluids: instantly change shape when applied an magnetic charge;
   - Magnetostrictive: are ferromagnetic materials that change their magnetization under stress or shape if subjected to a magnetic field;
   - Magnetocaloric: when exposed to a changing magnetic field they undergo reversible temperature changes;
   - Magnetorheological elastomers: consist of regular elastomers filled with micron-sized magnetizable particles as iron;
5. **pH-change/solvent/moisture => chemo-**
   - Smart gels: while also being responsive to temperature, light, electric, magnetic and mechanical forces they are pH-responsive. They consist of fluids in a matrix of large and complex polymers which swell or deflate depending on the stimulus;
6. **Light => photo-**
   - Photochromic > change color > belong to the chromogenic group;
   - Photomechanical: change shape under exposure to light;
7. **Molecular or Biomolecular => molecular-**
   - E.g. gas sensing materials;
8. **pH => pH-**

- are sensitive to the environment's pH variation by means of a change in volume or change in color (halochromic).

Due to being sensitive to external stimuli, most SRMs should be well suited for sensing applications. As we will see, some of these SRMs are already used in mostly actuation, sensing and energy harvesting applications.

Another useful categorization to do is of functions. All of the functions below are already being studied some of which directly for MFMS and which will be presented throughout the next chapters.

Functions/characteristics that future multifunctional composites ought to have:

1. Autonomy
   - Self-healing/repairing;
   - Self-powered;
   - Self-monitoring/diagnostic/sensing;
   - Self-assembling;
2. Highly tailorable properties;
3. Structural;
4. Active sound/vibration damping;
5. Actuation and ability to engage in shape-changing;
6. Electrical/Thermal Isolation/Conductivity;
7. Heating and cooling;
8. Electromagnetic interference (EMI) shielding;
9. Radiation protection, including lightning strike;
10. Light emission;
11. Energy storage;
12. Environmental: environmental remediation ability, recyclability and biodegradability;
13. Bio/human-related: bio-compatibility, non-toxic, able to change sensations related to the physical senses of human and other animals;
14. Chemical reaction functions: as catalyst, selective permeation;
15. Flame retardancy;
16. Information storage/processing capabilities;
17. Being able to be selectively functional: e.g. of energy absorbing plastics [37];
18. Levitation and movement inducing;
19. Intelligence.

Having presented this overall picture of MFMS it's now time to zoom into a bit more detail. In the following chapters we're going to review the state-of-the-art of several

MFMS, being the currently most important ones carbon-based nanocomposites, functionally graded materials, piezoelectric materials, and shape memory materials. Let's start with the first ones.

2.3 Carbon Nanomaterials

Graphene, **carbon nano tubes (CNTs)**, **carbon nano fibers (CNFs)**, are different spatial configurations of carbon atoms covalently bonded, as illustrated in **Fig. 11**, and have recently been the focus of a lot of research worldwide. This is because of an unusual combination of great mechanical, thermal and electrical properties. There are other possible carbon-based fillers for composites such as other carbon fullerenes shaped as hollow spheres and ellipsoids, and carbyne but they are comparatively under-researched. However, of those carbyne seems to be promising. Liu et al. [38] have predicted from first principles that this material has the highest specific stiffness and strength of any known material.

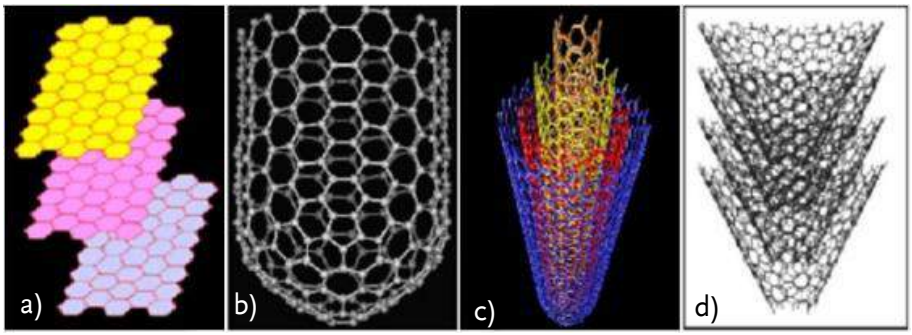


Fig. 11 – a) carbon nano wall or graphene; b) single walled CNT; c) multi walled CNT; d) carbon nano fiber. Adapted from [39].

There have been many papers presenting the mechanical characterization of these carbon nanomaterials [40-47] which unfortunately have seen highly variable results due to the difficulties in performing the required tests at the nanoscale, forcing many scientist to resort to indirect ways of measuring. This discussion was further detailed by Shokrieh et al. [44]. If we were to take a few representative values, CNTs would have 1 TPa < E < 1.8 TPa and 11 < σ_r < 150 GPa [40] and would be best thermal conductors currently known having a maximum thermal conductivity of 6600 W/mK for an individual SWCNT and > 3000 W/mK for an individual MWCNT, which is at least twice of diamond's, and a maximum electrical conductivity of ~300 MS/m for SWNT and > 0.1 MS/m for MWNT while revealing superconducting properties at low temperature [48]. Graphene has very similar properties [47], which makes sense seeing that a SWCNT is nothing more than a rolled graphene layer into a seamless cylinder. Moreover CNTs, graphene and CNF are of a very small size. Whereas traditional fillers generally fall on the mesoscale, these fall on the microscale and nanoscale for the lengths and diameters respectively.

It's possible, for example, that in nanocomposites the small size of the reinforcements overcome the microscale defects in composite materials. Also, because they are at the nanoscale, they are susceptible of reaching far greater surface **area to volume ratio (A/V)** than micro fillers. Also contributing to this advantage is that both CNTs and graphene have either very low (<< 1) or very high (>1) aspect ratio which also further increases their A/V ratio (**Fig. 12**). This ratio is one of the main reasons to develop nanocomposites. This is because a high interface region means high adhesion and high efficient transfer of stress across the composite components. This also means that for the same desired effect, a less amount is required of the filler with higher A/V. Here graphene has the upper hand over CNTs when embedding in a polymeric matrix, as they have a higher A/V because polymer molecules can't access the small opening of CNTs, and thus only the exterior area of the tubes contacts with the matrix.

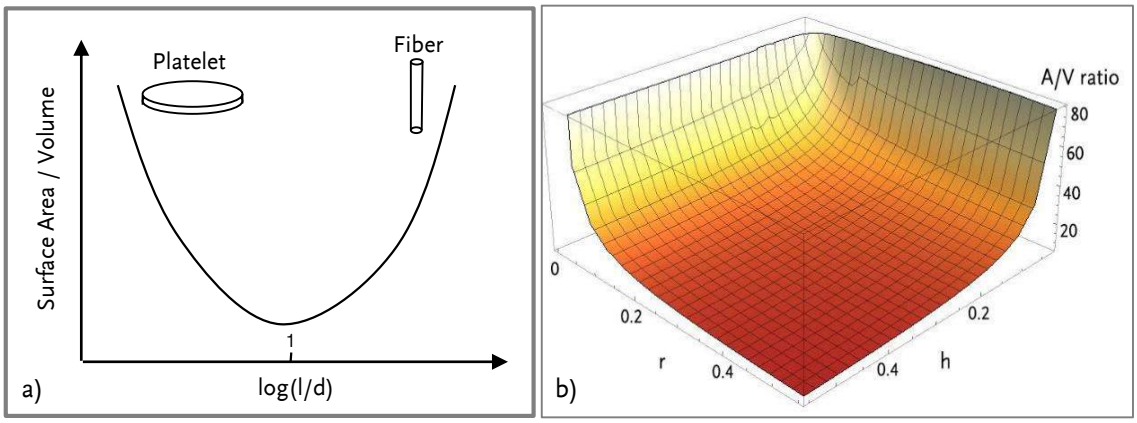


Fig. 12 – a) Variation of the ratio of surface area / volume (A/V ratio) against aspect ratio l/d and b) A/V ratio for a cylinder with its radius and height. Created with WolframAlpha.

For these reasons, i.e. extremely good mechanical, electrical and thermal properties and high A/V ratio, there is a keen interest in reinforcing materials with carbon nanomaterials to enhance their properties. Composites with polymer matrices have seen the most interest from the scientific community as a literature survey reveals (**Fig. 13**). This can be attributed to the relative ease of processing of polymers which don't require high temperatures for consolidation and also because of their inherent low density, which makes them fit for forming high specific strength and modulus nanocomposites. This interest can also be attributed to the fact that fiber reinforced polymer matrix composites such as glass and carbon fiber, can also be reinforced by these materials resulting in a multi scale composite with even better properties.

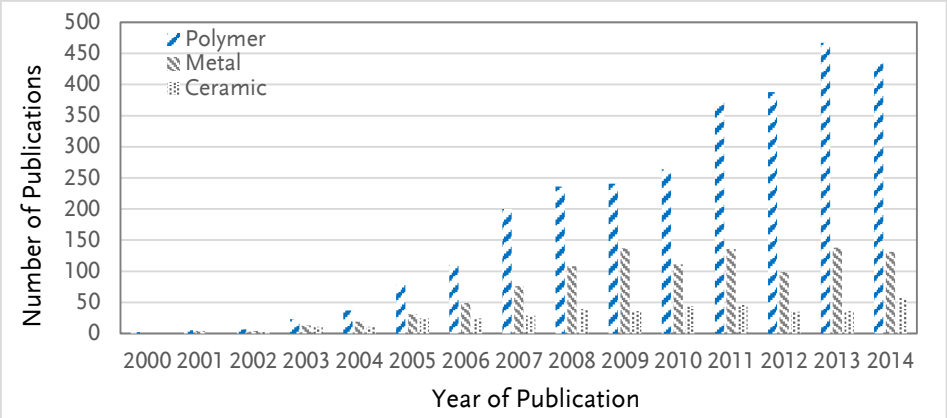


Fig. 13 – Number of publications on polymer/metal/ceramic matrix–CNT composite from EngineeringVillage.com.

Still, all three groups of materials benefit in different ways from being reinforced with carbon nanomaterials. Polymers see greatly improved thermal and electrical conductivity as well as increases in strength and elastic modulus when reinforced with graphene, CNTs or carbon nano fibers [47, 49-54]. Composites of ceramic matrixes, see an increase in toughness and electrical and thermal conductivity [48, 55]. Metal matrixes, most commonly based on Al, Mg, Cu and Ni have been reported to have increased resistance to corrosion, stiffness and strength [56-59]. Some representative examples can be seen in **Fig. 14**.

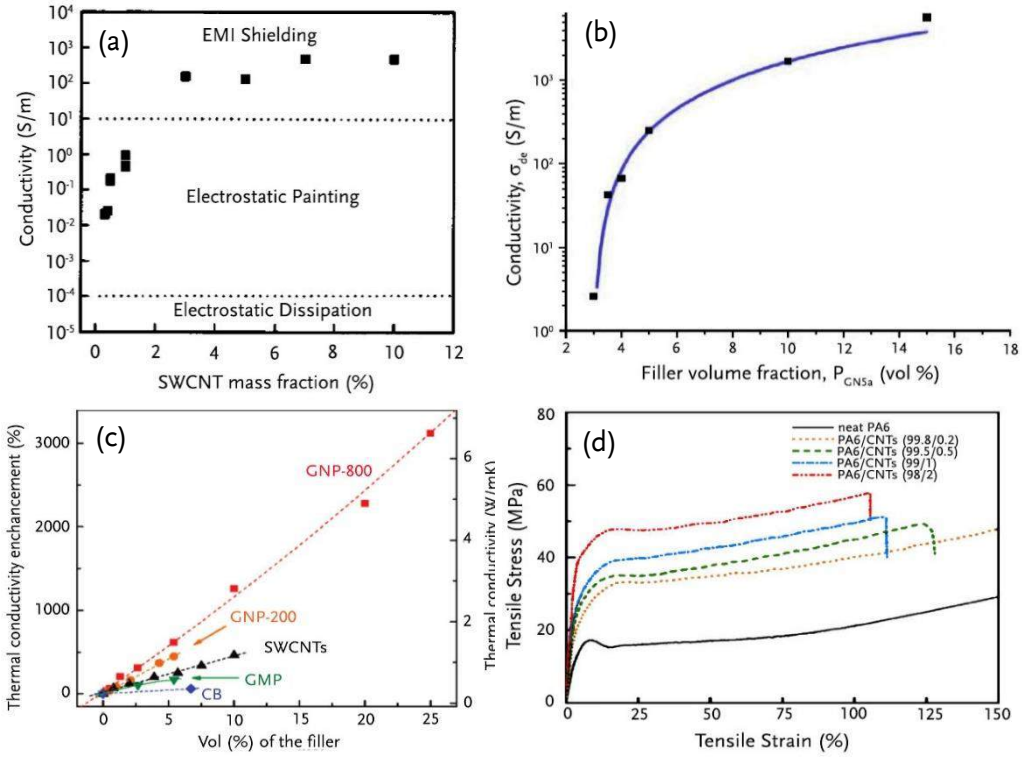


Fig. 14 – a) Electrical conductivity as a function of SWCNT mass fraction in a SWCNT–polycarbonate composite. The dashed lines represent the minimum conductivity necessary for the specified functions [60]; b) Electrical conductivity as a function of graphene volume fraction in a graphene–alumina composite. Adapted from [55]; c) Thermal conductivity of epoxy based composites as a function of

filler, carbon black (CB), graphitic micro particles (GMP) and nanoplatelets (GNP) and single walled CNTs (SWCNT). Adapted from [61]; d) Stress–strain curve for a nanocomposite of PA6 polymer matrix and different CNT filler concentrations, adapted from [62]

Though it isn't yet understood why, the incorporation of nanofibers or nanoplatelets also reduces maximum heat release rate (**Fig. 15 a**), which is important for minimizing flame propagation to adjacent areas. Still, the total heat release remains the same, as the area under the curve reveals.

Kaul et al. [63] have presented a thermal interface material for load bearing structures with thermal management needs, such as super and hypersonic vehicles, a composite of vertically aligned CNT reinforced epoxy where the CNT provide through the thickness thermal conductivity and the epoxy transmits the loads.

Because of these interesting properties, new functions can be added to the reinforced material, including actuation [64, 65], strain and chemical sensing [66, 67], energy harvesting [68-70], energy storage [69, 71], protection from corrosive agents [72], flame retardant properties [73] and environmental remediation and/or protection [74-76].

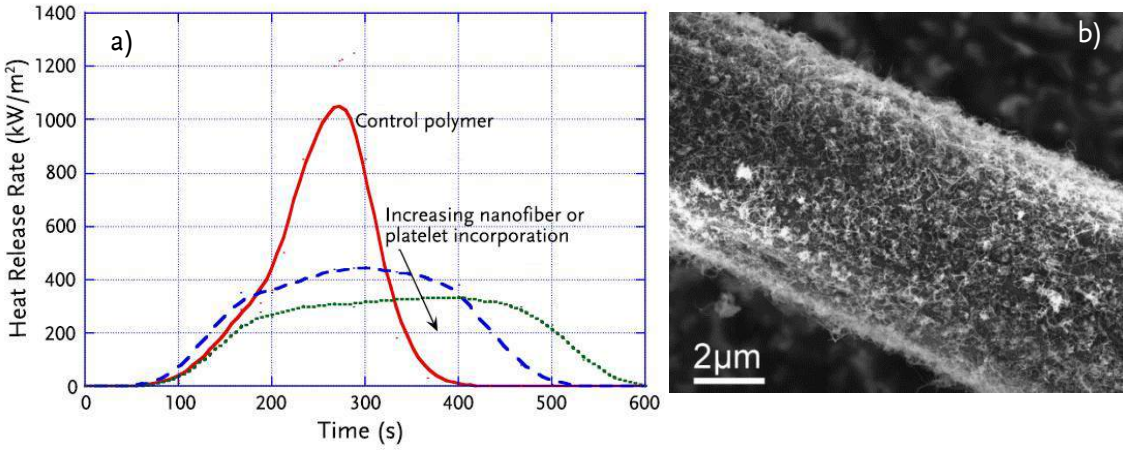


Fig. 15 – a) Reduction in maximum heat release rate due to incorporation of nanofiber or platelet [77] ; b) Carbon fiber after growth of CNTs on its surface[78].

Given than the most often used composites have polymer matrix materials, in aircrafts where electrical conductivity is needed in certain parts to transfer electricity from thunders, the poor conductivity of polymers has to be compensated by the addition of more parts whose sole function is to transfer lightning strikes' electricity. Polymer matrix nanocomposites with carbon-based fillers are being investigated as a possible replacements for regular polymers typically used in composites' matrixes [79].

The piezoresistivity of CNT-polymer composites is very promising because it opens an alternative to the conventional piezoelectric materials used to actuation and sensing to be embedded in active MFMS. A review was published by Alamusi [66] on this subject.

Scientists and engineers are also trying multiscale reinforcements, that is, reinforcing composites with regular fibers and CNTs [78, 80, 81]. This multiscale reinforcing, may be such that the CNTs are dispersed along the carbon fibers themselves (**Fig. 15 b**).

One of the areas directly concerning MFMS is structural health monitoring where they are being extensively researched [82, 83].

Song [84] presented a self-sensing laminated composite, as illustrated in **Fig. 16**. Amongst the conventional fibers the author stitched a tough electrically conductive CNT thread. The composite was able to sense damage and strain. Since nanotubes have piezoresistive properties its piezoimpedance changed when the beam strained or it would see a sharp increase if it fractured.

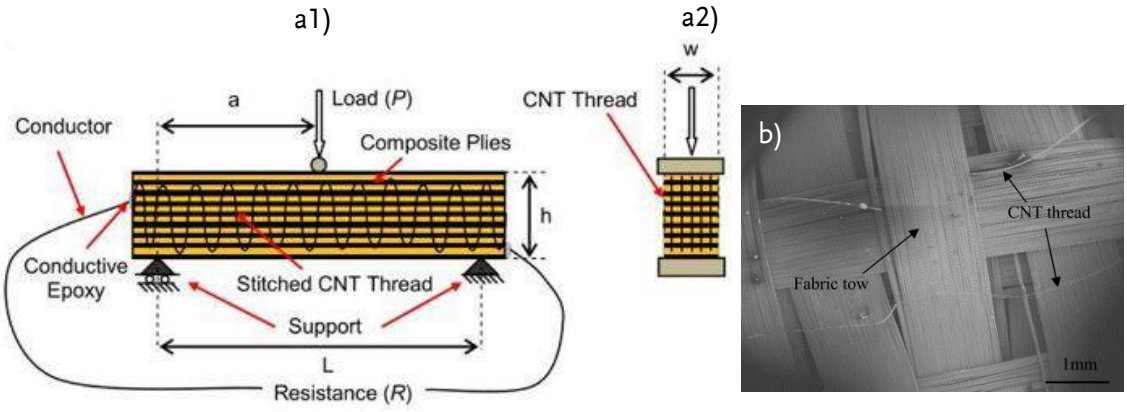


Fig. 16 – a1) Drawing of the longitudinal cross-section of beam composite beam with delamination detection and strain sensing capability. When delamination occurs, the CNTs break increasing the circuit's resistance; a2) transverse cross-section of beam; b) A plain carbon fiber ply with the CNT thread stitched [84].

Baltopoulos et al. [85] proposed a solution where the CNTs are dispersed in the composite, functioning as a network of electrically conducting elements, and that when a crack or delamination occurs, their electrical conductivity is disturbed allowing the localization of said damage (**Fig. 17 a**).

These nanomaterials are also being extensively used for adding energy storage function. For example, Hu, et al. [86] developed an ink infused with carbon nanotubes and silver nanowires that can be painted onto several surfaces giving that surface energy storing capabilities.

Liu et al.[87] attempted to creating a structural battery where the polymer cathode is a carbon nanofiber-reinforced polymer, instead of the regular cathode on polymer Li-ion batteries (**Fig. 17 b**). Also the researchers used a solid-state polymer electrolyte instead of the conventional organic liquid ones. The separator region was also reinforced with non-conducting fibers. However, the Young modulus was only 3GPa and it had low energy density compared to conventional Li-ion batteries.

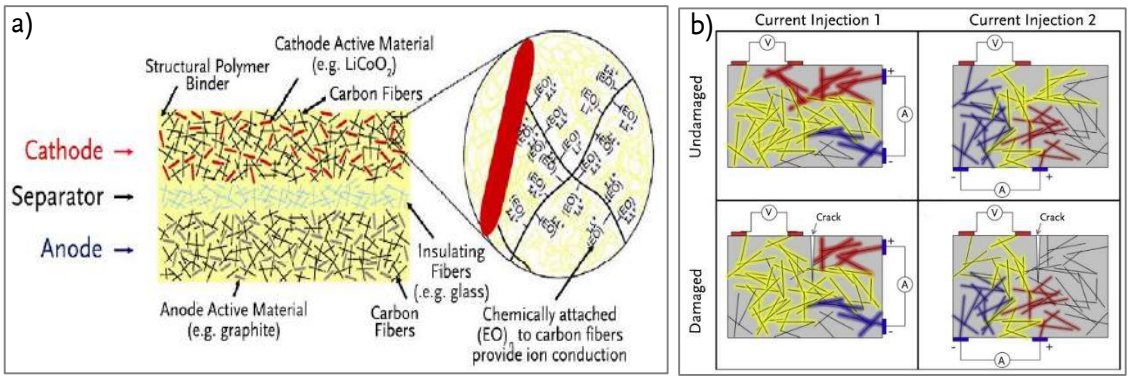


Fig. 17 – a) Crack localization by electrical resistance tomography in a CNT reinforced composite. Adapted from [85]; b) An illustration of the constitution of a structural battery developed by Liu et al., adapted from [87].

Yu, et al. [88] developed a supercapacitor composed of graphene and CNT that they claim is flexible enough to be woven into clothing and with potential to be powerful enough to serve as a real alternative to conventional batteries. The hybrid fiber has a huge capacitive surface area of 396 m^2/g which results in a capacitance of 300F/cm^3 and a power density of 6.3mW/m^3 which would be comparable to a 4V 500mA Li-ion battery. They also developed a scalable method to continuously produce the fibers allowing future mass production.

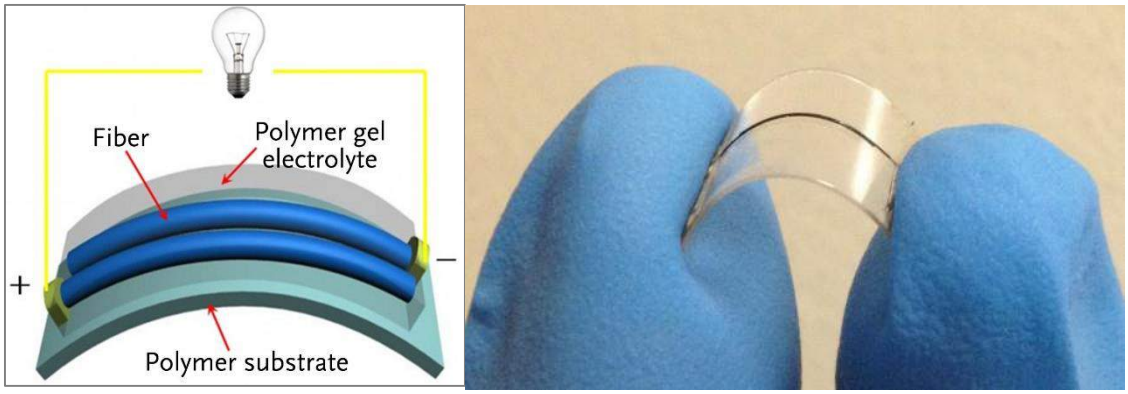


Fig. 18 – The flexible supercapacitor made of graphene and CNT developed by Yu et al. [89].

Loh et al.[90] showed a composite material of multilayered carbon nanotube-polyelectrolyte produced to monitor strain and corrosion, where the type of polyelectrolyte determined the sensitivity to pH and the concentration of CNTs determined the sensitivity to strain.

Additionally this multifunctional structure can also be used to produce multifunctional composites for anti-corrosion coatings, biological implants, and thermal/electrical interface materials with high strength [91, 92].

Lightcap et al. [93] briefly overviewed advances in sensing, energy conversion, and storage applications incorporating graphene-based composites.

Another promising application is coating other materials with graphene. In a collaboration between Portuguese an UK universities, Neves et al.[94] have successfully coated PP and PLA fibers with a transparent flexible single layer of graphene. They 'CVDed' the material onto a copper foil, then spin-coated PMMA on the Cu/graphene substrat, removed the copper by etching. The graphene was transferred to the PP fibers and finally the PMMA with acetone. The resulting electrically conducting fibers had electrical resistivity not much greater than that of graphene.

It has been known that water flow over CNTs generates a voltage in the flow direction. However that voltage are no greater than a few millivolts. By using molecular dynamics simulations Dhiman et al. [70] discovered that flowing water over graphene causes the ions in the water to drift along the flow direction, while sticking to the graphene's surface (**Fig. 19**). This movement drags the free charges present in graphene along, resulting in an internal current and a power density of 175W/m^2.

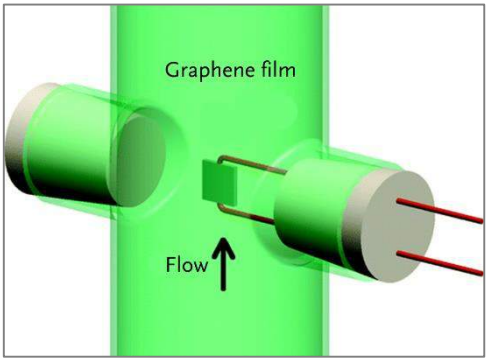


Fig. 19 – An illustration of a graphene film harvesting energy from flowing water[70].

Despite all this interest and investigation in these materials, their implementation in useful applications has been slow and their commercialization elusive. The main challenge lies on the manufacturing. For example for proper homogeneity of CNTs and CNFs there needs to be a good dispersion on the matrix but they tend to hold together forming bundles due to van der Waals forces [67]. Sometimes it also desirable to have the nanofillers aligned for example for applications that take advantage of anisotropic thermal, electrical and mechanical properties [95], however that is even harder to accomplish and there has been a lack of research comparing to the research existing related to solving the dispersion problem. The lack of control over dispersion and alignment of the nanofillers makes reproducibility hard, and also significantly reduces the composite quality. Another issue is obtaining a strong interface between the CNTs and the matrix, to obtain proper load transfer, for without it it's not possible to utilize the exceptional properties of CNTs. Then there's the problem of obtaining high purity, the lack of which can result in significantly reducing the resulting CNTs properties. In the usual methods of production – chemical vapor deposition, laser ablation and arc discharge – there are residual particles that are left after the process is complete, and purification still remains a challenge [96]. Finally there still needs to be an evaluation concerning CNTs and graphene

toxicity, which has been hard to determine due to the small scale involved. Some reviews have been published but they are of mixed results [67], such as the reinforcing of CNT having been shown to reduce the composite mechanical properties compared to the pristine material [41].

Slowly but surely, 3D printing is also showing its advantages in multifunctional composites. Compton et al. produced the first 3D-printed cellular composite of CNF-epoxy with very good mechanical properties. Until then, 3D printed polymers comprised thermoplastics and UV-curable resins. It was inspired on balsa because of its fabulous specific bending stiffness (E/ρ^2) and specific bending strength $(\sigma^{\frac{2}{3}}/\rho)$ (**Fig. 20**).

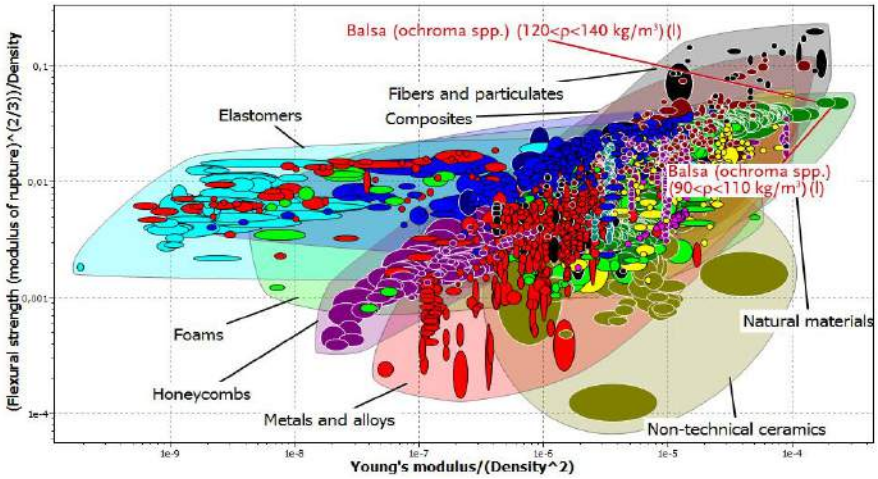


Fig. 20 – Specific bending stiffness and strength of balsa compared to other materials. Created with level 3 [97].

The mix itself is composed of epoxy resin mixed with SiC whiskers, CNFs and some additives to achieve the desired rheological properties and it was printed with a 3D-extrusion-printing method that allowed the alignment of the carbon nano fibers during the printing process (**Fig. 21 b**).

The Young's modulus increased by 9x compared to the pure epoxy resin (they compared with transversely aligned with longitudinally aligned) and slightly increased ultimate tensile strength of 92MPa for the longitudinally aligned specimen (**Fig. 21 c**). The authors correctly recognize the possibilities in obtaining highly tailorable functionally graded materials, to be discussed in the following chapter. By changing the fillers, say CNTs, several functionalities can be added.

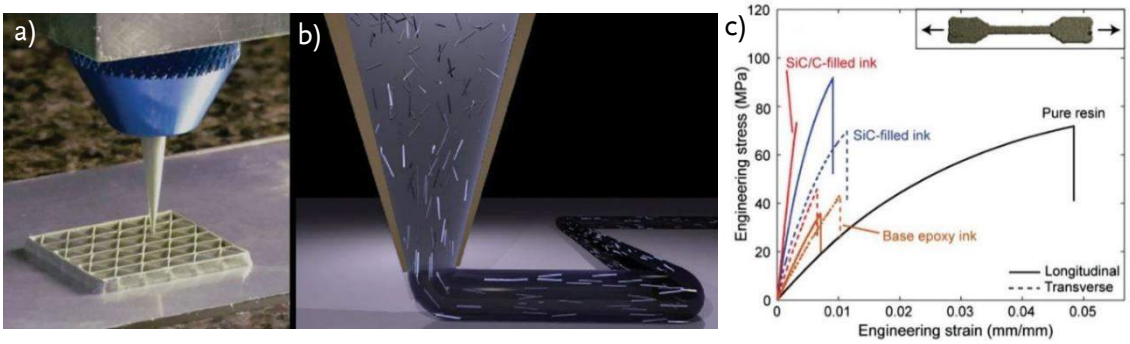


Fig. 21 – a) 3D extrusion printing of honeycomb composite; b) Illustration of the alignment of the fibers through the printing nozzle during ink deposition; c) Representative tensile test for the 3D-printed tensile bars with various compositions [98].

Graphene too, has had troubles with mass manufacturing whose large-scale graphene-like materials have shown inferior properties. Recently though we are seeing some solutions, such as the one proposed by Vlassiouk et al. [99] who have shown the feasibility of producing 5x5cm continuous sheets of single-layer graphene grown by chemical vapor deposition. Still, more work is needed in this area. Other papers claim breakthroughs. For example, Paton et al. claim a new mass manufacturing method of graphene based on the scotch tape method [100] and Polsen et al. on CVD [101]. The former consists in putting graphite in water and exciting it with a spinning rotor, which separates the layers of graphite from each other, then adding a compound to the mix to keep them that way. The latter consists in using a vacuum chamber where a carbon containing vapor reacts with a substrate that is moving at 25mm/min. There are two zones in the chamber, the first prepares the substrate for the deposition, and in the second the deposition takes place and a very uniform and high quality single layer of graphene is created. They are currently studying how to make the movement speed faster so that quality of the resulting graphene maintains at higher speeds.

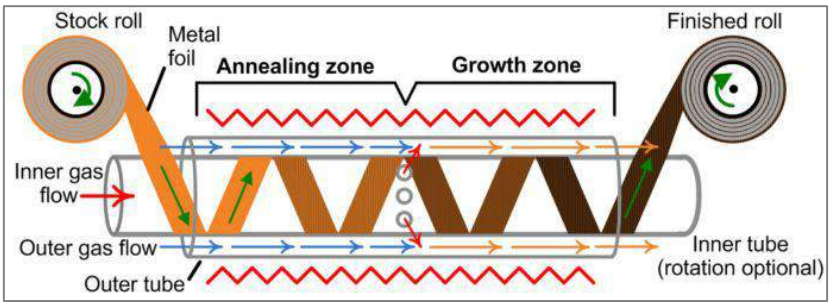


Fig. 22 – Novel manufacturing method proposed by Polsen et al. for mass manufacturing of graphene [101].

2.4 Functionally Graded Materials

Functionally graded materials (FMGs) are composite materials where there isn't a clear interface between the different materials because the change from one material to the other is gradual or graded. For example ceramic-metal FGMs such as the one in **Fig. 23**

can have the high fracture toughness and thermal conductivity on the metal side and the hardness and thermal stability on the ceramic side. The gradation can take many forms, as shown in **Fig. 24**.

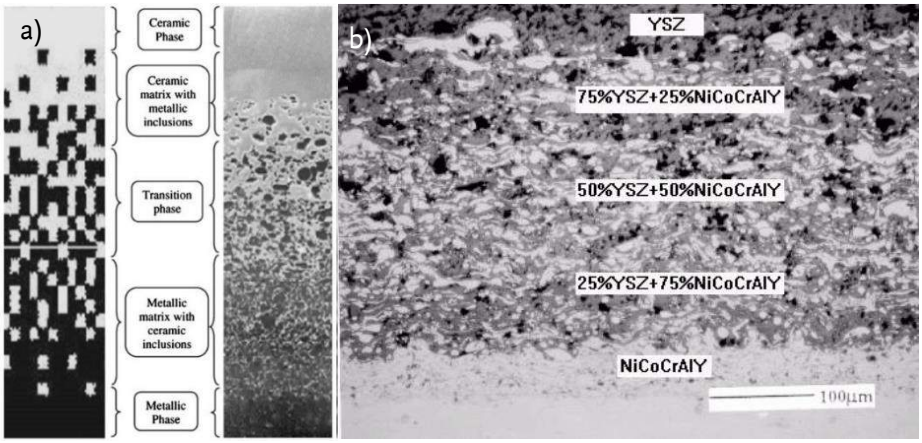


Fig. 23 – a) Microstructure of two ceramic–metals FGMs [102]. b) a FG ZrO_2/NiCoCrAlY thermal barrier coating obtained by plasma spraying [103].

Also because there are no well-defined interfaces or boundaries between the different materials but only a smooth transition between them, there are good chances of for example reducing thermal and mechanical stress concentrations that occur in traditional composites, and where failure is initiated [102].

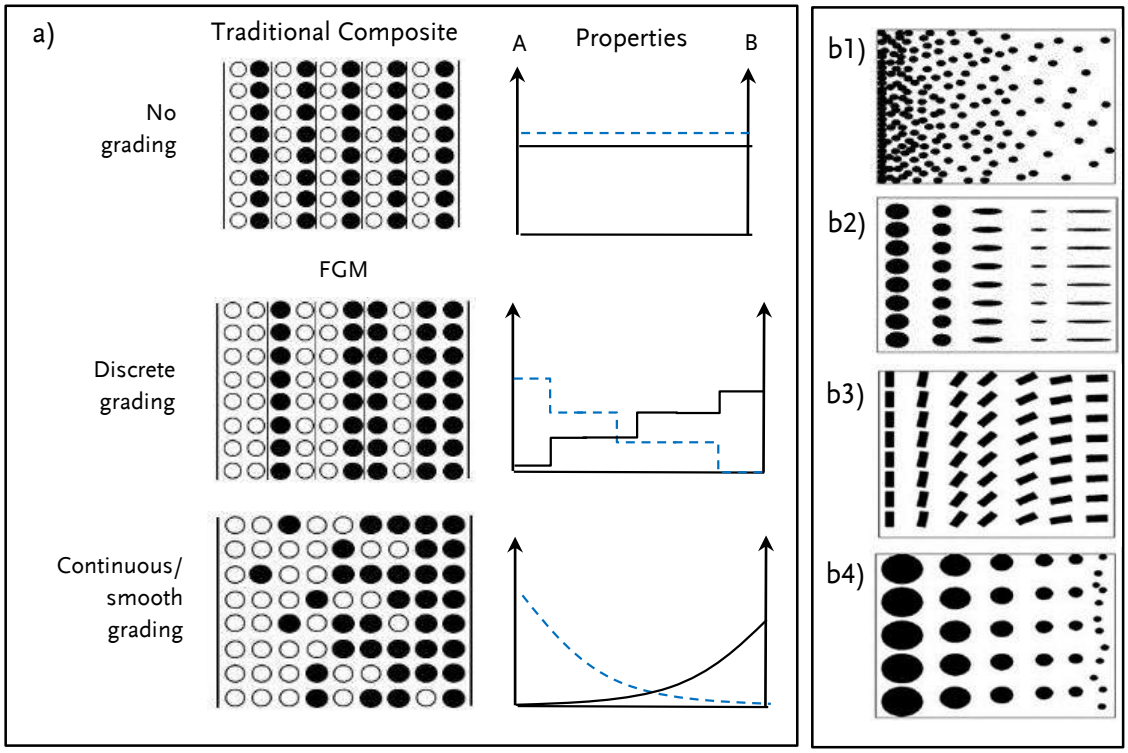


Fig. 24 – a) Comparison between traditional composites and FGMs concerning the grading and properties. Types of FGMs concerning the nature of the gradient: b1) fraction gradient, b2) shape gradient, b3) orientation gradient, b4) size gradient. b1)–b4): [104].

This smooth transition reduces the high local inter-laminar stresses in common composites which result in the separation of layers and the consequent degradation of several mechanical properties leading to final structure failure.

This is a field that has seen a steady increase in interest from the scientific community having quadrupled the number of journals since 2000 (**Fig. 25**).

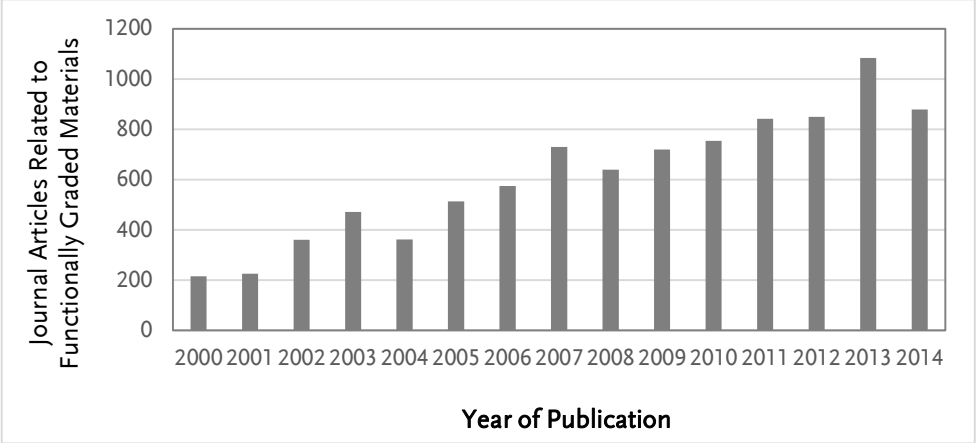


Fig. 25 – Journal articles related to FGMs, from EngineeringVillage.com, March 2015.

FGMs were originally designed for use as thermal barriers in fusion reactors and aerospace structural applications, and later on in structural parts at very high operation temperatures.

Recently the research about FGMs is focused on:

- FGMs subjected to thermal and mechanical loading [105, 106];
- Modeling and numerical simulation of loading parts made of FGMs [107, 108];
- Fracture properties and crack propagation/analysis [109, 110];
- Using piezoelectric materials and CNTs along with FGMs [104, 111];
- Improving and discovering better manufacturing processes [102, 112].

There is a recent interest growing which is in making FGMs where the concentration of CNT is graded. These materials show improvements relating to weight, electrical conductivity, dimensional stability, flame retardancy and strength [111]. These can potentially be used as gas adsorbents, actuators, catalyst supports, probes, chemical sensors, nanopipes, nano-reactors among others [104].

FGMs can also be used at interfacial zones to improve bonding strength, improve environmental resistance and to reduce crack driving [110].

Wang et al. [105] introduced a thermal protection system, a perspirable skin, made of, among others, a FMG of ZrW_2O_8 and ZrO_2, where with an increase in temperature a gaps are formed in the FGM with the help of a buckling action, allowing the passage of a cooling gas.

Other current applications include [102, 113]:

- Aerospace: rocket components such as rocket nozzles (TiAl-SiC fibers), thermal protection systems for atmosphere reentry vehicles;
- Medical: artificial bones, skins, dentistry;
- Energy: solar cells, sensors, thermoelectric generators, heat exchanger panels (Be-Al);
- Communication: optical fibers, lenses, semiconductors;
- Miscellaneous:
  - Engine cylinder liners (Al-SiC);
  - Brake rotors and leaf springs (e-glass-epoxy);
  - Drive-shafts (Al-C);
  - Cylindrical pressure hull (graphite-epoxy);
  - Sonar domes (glass-epoxy).

The main challenges to overcome for the reduction of cost and implementation of these materials are mainly related to manufacturing. Jha et al. [102] have reviewed the current state-of-the-art on fabrication processes, the current models to estimate the FGM properties and a compilation of recent research on FG plates and present the need to focus more effort on improving the current most promising manufacturing method which is solid freeform.

2.5 Piezoelectric

Piezoelectric materials are materials that generate an electric potential in response to an applied mechanical stress – the **direct piezoelectric effect** – which can be used for sensing or energy harvesting, and when applied an electric field to the material it will either change shape or generate mechanical stress – **inverse piezoelectric effect** – which can be used for actuation and shape control.

In practice this means that if we apply a force to a piezoelectric material, it will develop a positive charge on one end and a negative charge on the other end. If we connect the two ends, current flows.

Despite there existing several active materials such as shape memory alloys, magnetorheological fluids, electrostrictives, etc., piezoelectric materials remain currently the most widely used active material. This is because they are capable of actuating or sensing at frequencies from about 1Hz to the MHz range with relatively linear behavior. Moreover, piezoelectric materials have high stiffness which provides them with strong voltage dependent actuation.

The most often used piezoelectric materials are **polycrystalline ceramic** (PZT, $PbTiO_3$, $BaTiO_3$), **single crystals** (SiO_2, $LiNbO_3$, LiTaO) and **polymeric** (PVDF, co-polymer) and they take the form of **monolithic**, **thin films** [114], **wafers** [115] and (**nano**)**fibers/wires**,

[116-121] which can be **hollow** [122-124] and arranged as **macro and active fiber composites** [125, 126] (***MFCs***[1] and **AFCs**) or **1-3 Composites**. Comparatively, the piezoelectric ceramics are more brittle but have larger actuating forces, whereas the piezoelectric polymers withstand higher deformations and so are better fit for shape changing applications or irregularly shaped parts. Traditionally the ceramics have been the most used, especially PZT, and more specifically in the monolithic form. This is mainly due to low cost, ease of manufacturing, high coupling efficiency, that is, high efficiency in converting electrical to mechanical energy, chemically inert, high operating temperature and high sensitivity (for sensing), among other qualities. However, it is very brittle and therefore requires extra care when being handled. It has also very poor conformability to curved surfaces generally requiring extra manufacturing steps so that in that can be used.

A way that the fragility of the piezoceramics has been partially overcome while also increasing the flexibility of the material is by having them in the form of fibers. Typically crystalline materials have much higher specific strengths in the form of fiber because the volume fraction of flaws diminishes. Then by embedding those fibers in a tough polymer-matrix we can increase toughness and flexibility of the composite [127]. This was why AFCs were developed, and then later the *MFCs*. Between the two, the rectangular cross-section of the *MFC* fibers as opposed to the circular of the AFCs, allow for a greater transfer of the electric field from the electrodes to the PZT fibers due to the increased contact area and are easier to manufacture, align and space out correctly, and have up to 150% of the strain of AFCs (**Fig. 26**). For these reasons, *MFCs* realized commercial licensing and mass production, something never achieved by the AFCs. A more detailed comparison can be found in the literature [128].

Piezoelectric fibers also find use outside of *MFCs* and seem very promising because they have the most potential to be well integrated (resulting in a type II composite) into a material without being parasites and they can also reduce the typically high voltages required by *MFCs* for actuation purposes.

[1] As to not change acronyms I decided to keep both meanings for MFC (macrofiber composite and multifunctional composite) but to not induce the reader into confusion, *MFC* meaning macrofiber composite will be always typed in *italic*, as opposed to multifunctional composite MFC.

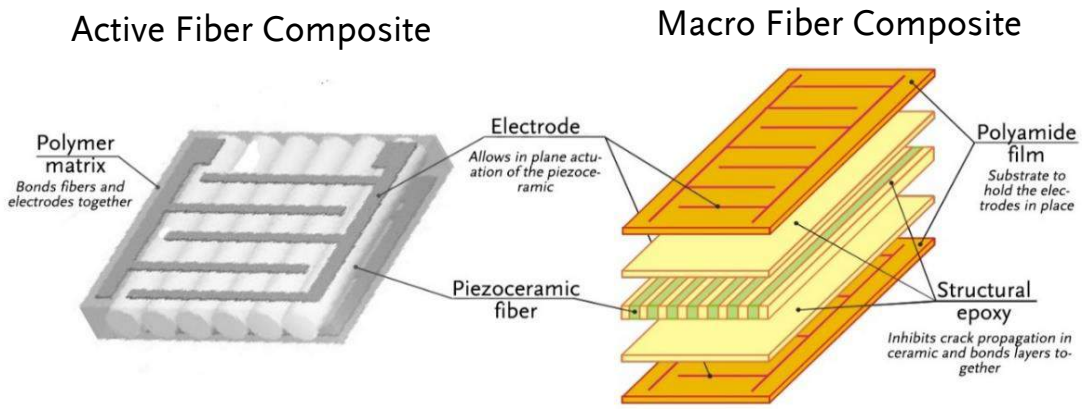


Fig. 26 – Constitution of a typical AFC and a *MFC*. Adapted from [128, 129].

A good example was developed by Lin and Sodano [130, 131] which consisted of piezoelectric structural fibers that can be laid up in a composite material to perform sensing, actuation and load bearing capacity. The structural fiber was made of a piezoelectric material as an interface between an interior carbon fiber and an exterior piezoelectric material, as illustrated in **Fig. 27 a**. Guillot et al. [132] also developed a Teflon-FEP coated PZT hollow fiber for sensing and energy harvesting purposes (**Fig. 27 b)** revealing a flexibility that wouldn't be possible had it not been coated (**Fig. 27 c)** and producing twice as much energy density as the current state of the art *MFC*s.

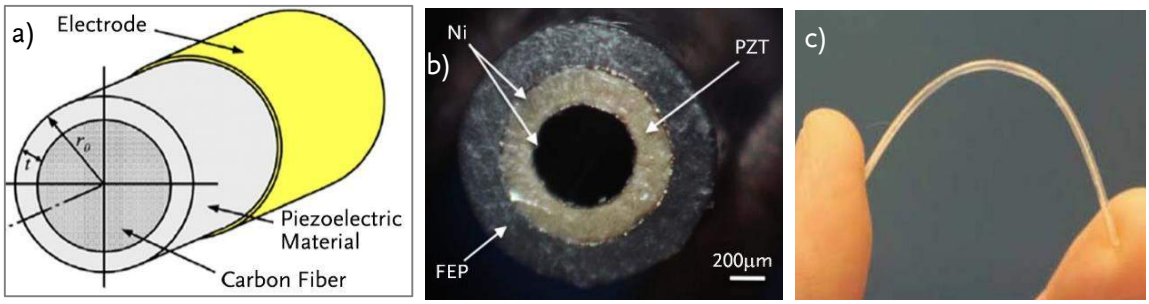


Fig. 27 – a) Hybrid structural-actuating fiber [130]; b) One mm diameter hollow PZT fiber coated by Teflon-FEP c) in bending. Adapted from [132].

Next, I discuss some of the fields where piezoelectric materials currently find use and their applications concerning MFMS.

Actuation

Using the inverse piezoelectric effect, it is possible to use piezoelectric materials for actuation. They are commercially available and are currently used for this purpose in a variety of fields including industrial, automotive, medical, aviation, aerospace and consumer electronics applications.

However, even though we're progressing towards smaller and thinner options, such as hollow fibers, nanowires/fibers and *MFCs*, many of today's piezo actuators are still bulky monolithic devices. When integrated in a material the monolithic piezo materials

have clearly parasitic effects, i.e. they don't contribute to the load bearing capacity of the structure and may actually diminish it because of stress concentrations generated in the structure by their inclusion. This is why fiber-based piezo materials are being extensively researched as replacements, as they are better suited for integration in composites. Multiscale analysis [133] as well as finite element analysis [134-136] have been made on the subject of smart structures containing piezoelectric fiber-reinforced composite actuators. However due to their traditionally fragile nature and because they are but one of the many other possible materials for use in active and semi-active structures [137], piezoelectric fibers have seen more total research in sensing and energy harvesting applications than actuation.

However with the development of *MFCs* and the improvements in manufacturing at the nanoscale, this is a field in clear expansion, and the following cases reveal success. *MFCs* are composed of unidirectionally aligned rectangular piezoceramic fibers bonded by a polymeric matrix, and sandwiched between interdigitated electrodes (**Fig. 28**). This arrangement of electrodes exploits the d_{33} electro-mechanical coupling allowing for greater efficiency. Because they are thin and flexible, they can easily be coupled to the surface of other parts, and allow for several actuation types (**Fig. 28**).

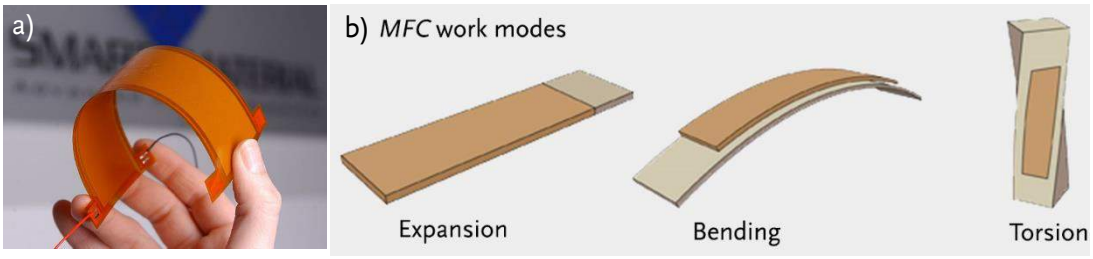


Fig. 28 – **a)** Picture of an MFC showing its high flexibility [138]; **b)** *MFCs'* work modes. Adapted from [139].

One example of where this configuration is desired is in shape morphing structures which have a great appeal for components for aircrafts, where morphing parts could replace the need for parasitic heavy actuators as we saw in the introductory chapter.

Li et al. [140] have presented an approach for increasing aerodynamic performance, such as increasing lift, reducing drag and improving roll performance, by using several *MFCs* distributed on the aircraft wing surface that control the wing's mechanical deformations.

Damping systems based on piezoelectric materials have been developed and established in several engineering fields. For example Chen et al. [125] developed a vertical fin for a F/A-18 to control the first mode of torsional vibration which had MFCs on both sides (**Fig. 29 a**). It resulted in a reduction of the dynamic strain by 41% and dynamic acceleration by 43%.

Some other applications have also already been developed such as a piezoelectric actuator for a smart projectile fin [141], flapping wings using *MFC* actuators (**Fig. 29 b-d**)

[142], shape-changing of airfoils [143], with end-goal of flight control [144], for improving hydrodynamic performance [145], and to suppress and/or control structural vibrations [146, 147] and in aiding for other self-healing mechanisms[148]. These are just a few examples of the topics where they are being applied.

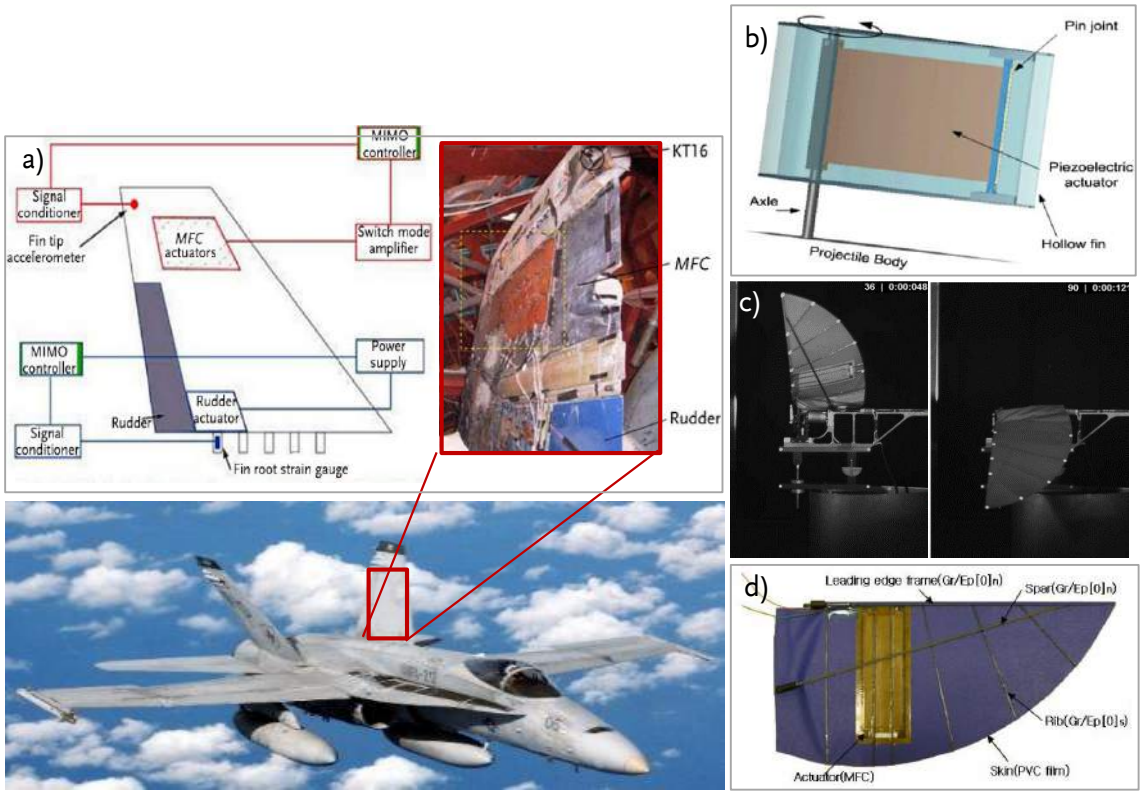


Fig. 29 – a) A piezoelectric–composite–based damping system for a vertical fin of the F/A–18 [125]; b) *MFC* actuator for a small projectile fin [141]; d) A smart flapping wing actuated by an *MFC* and c) it's motion mimicking birds' flight [142].

Sensing

By using the direct piezoelectric effect, it is possible to use piezoelectric materials as sensors. Even though piezoelectric sensors have several commercial applications, like commercial piezoelectric actuators, many are used as independent devices. Here we are interested only in those that are capable of belonging in a MFMS. An area where such is implemented is on **structural health monitoring (SHM)**, both for sensing vibrations and static strain. So far most applications have been in the civil engineering field but there is a great interest in several other fields to use self-sensing materials. In composite structures the damage is many times internal and not visible on the surface, which makes it difficult to detect, because it requires advanced techniques such as thermography and ultrasonics, which require the use of specialized equipment. One of the ways a self-sensing mechanism can be implemented is through the use of sensor networks using piezoelectric materials embedded in the composites.

An example of this was presented by Lin and Chang [149] who produced and tested the Stanford-Multi-Actuator-Receiver-Transduction (SMART) Layer for the structural

health monitoring of a host composite. In this case it involved an array of networked PZT piezoceramic actuators/sensors which are embedded in a layer to be layed up in between carbon fiber/epoxy composite laminates, forming a multifunctional structure as shown in **Fig. 30**.

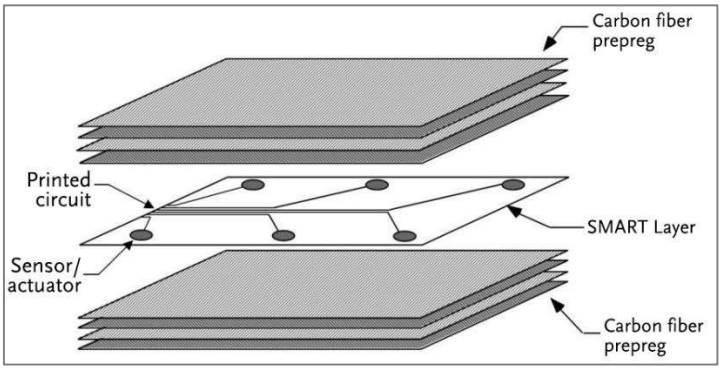


Fig. 30 – Illustration of the SMART layer for sensing in laminated composites [149].

This layer has already been used for the localization of impact damage by Haywood et al. [150]. Many other reports have also been published on the use of these kinds of artificial neural networks to study the data and assess their effectiveness in correctly characterizing the damage induced, namely the location, severity and type of damage in composite structures [151-156].

Boeing also recently issued a patent of an ink-based piezoelectric sensor for SHM for use in airplanes which could be deposited onto the surface of structures [157] but it seems more of a defensive measure as ink based piezoelectric powders is still a very weakly developed field, as there are very few papers published on the subject.

Instead of being directly used as sensors, piezoelectric materials can also be used as transducers in conjunction with sensors for SHM, such as the design proposed by Barazanchy et al. for aerospace composites [158].

Piezoelectric wafers, a lightweight and cheap solution, have also be used as active sensors embedded or attached to composite structures [115, 159, 160].

Besides SMART layer and wafers, more recently piezoelectric fibers have started being used as *MFCs* for sensing purposes [161-163]. These have been integrated in fiber reinforced composites as an initial stage for self-sensing composite structures. An analysis of the effectiveness of piezoelectric-fiber-based sensor to monitor the stress/strain concentration levels at the critical locations embedded inside composite structures was recently published [164] concluding that these have good sensitivity and performance compared to conventional strain gauges at low strain levels.

Energy harvesting/generation

Energy harvesting refers to harnessing energy from the environment and converting it into useful energy. Even though the ambient energy can take many forms, the one usually concerned when dealing with piezoelectric materials is vibration or strain, which take advantage of the piezoelectric effect of these materials. The use of piezoelectric materials in this field has been a topic extensively researched [121, 165-171] and seems to be the one where piezoelectric materials for MFMS show greater strength. In fact several piezoelectric materials, such as **ZnO** [172, 173], CdS [174], InN [175, 176], $NaNbO_3$ [177], **PZT** [178-180], $BaTiO_3$ [179, 181], $LiNbO_3$ [182], **PVDF** [118, 183], among others, have been employed for fabricating nanogenerators. I bolded the ones that, based on their state-of-the-art, seem to have the most potential and to be the most interesting for researchers. Of these, the most used one is PZT as it is the one that exhibits the greater piezoelectric effect [184]. PVDF is also very used because it is much more flexible, it is capable of straining at a much higher rate and has the highest known piezoelectric properties of any polymer [185]. ZnO is the easiest to manufacture in the shape of nanowires/nanofilms, which can take advantage of the nanoscale size effects, it has excellent piezoelectric properties along one of its directions, among other properties [186].

Sometimes energy harvesting is done with the purpose of powering the material so that it can regulate itself. There are many examples of the energy of vibrations being harvested to power a vibration control mechanism. For example, a concept and design was presented by Wang et al. [187] of a simultaneous energy harvesting, storage, self-sensing and with vibration control wing spar. The objective is a composite wing spar for a small UAV which harvests energy from ambient vibrations during normal flight as well as from sunlight and uses that energy for, among others, to regulate the wing vibrations. The design is seen below in **Fig. 31**.

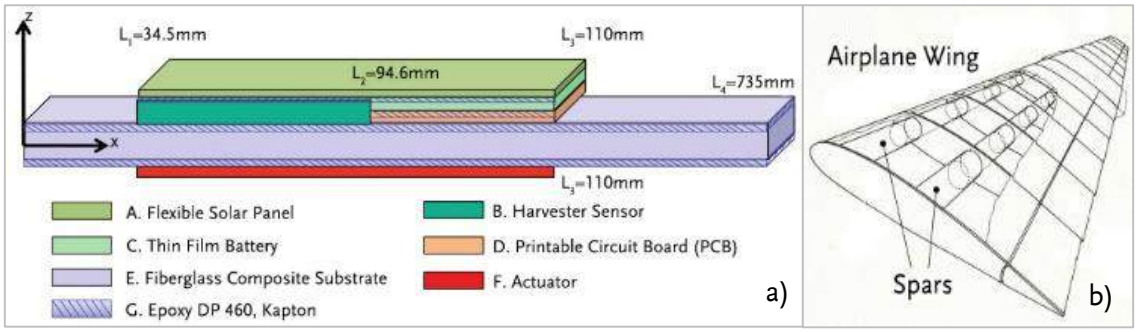


Fig. 31 – a) A design for a type I multifunctional wing spar with several functionalities including self-sensing, self-harvesting, self-storage, and self-control. Adapted from [187]; b) Spars of an airplane wing. Adapted from [188].

In his doctoral thesis [189] Wang implemented a piezoelectric-based system that uses the energy harvested to directly control the vibration response of a multifunctional wing spar, which would be able to harvest solar energy, store the energy in a thin film battery, self-control vibration and strain sense.

Traditional glass fiber/epoxy and carbon fiber/epoxy seem also to be viable choices for energy harvesting through the integration of piezoelectric materials. Tien and Good [190] produced such composites with PZT (**Fig. 34 a**) and concluded, after running numerical and experimental validation, that it has efficiency potential.

Using thin and/or bendable piezoelectric materials is one of the most promising research areas. This is because they have the highest potential for integration in other materials. One of the piezoelectric materials being extensively studied for this purpose is multilaminar polyvinylidene fluoride (PVDF) which can be produced as a thin layer and has been used and is being studied for interesting applications. For example Shenck et al. [183] scavenged 1.3mW of the energy dissipated in the bending ball of the foot by using a stave of PVDF in the sole of a shoe at a walking pace of 0.9Hz (**Fig. 32 a-c**).

A more recent attempt at the same objective, used electrospun PVDF sandwiched between a pair of conducting electrodes having managed to obtain 2.1mW at 210V and 45μA [118] (**Fig. 32 d-f**).

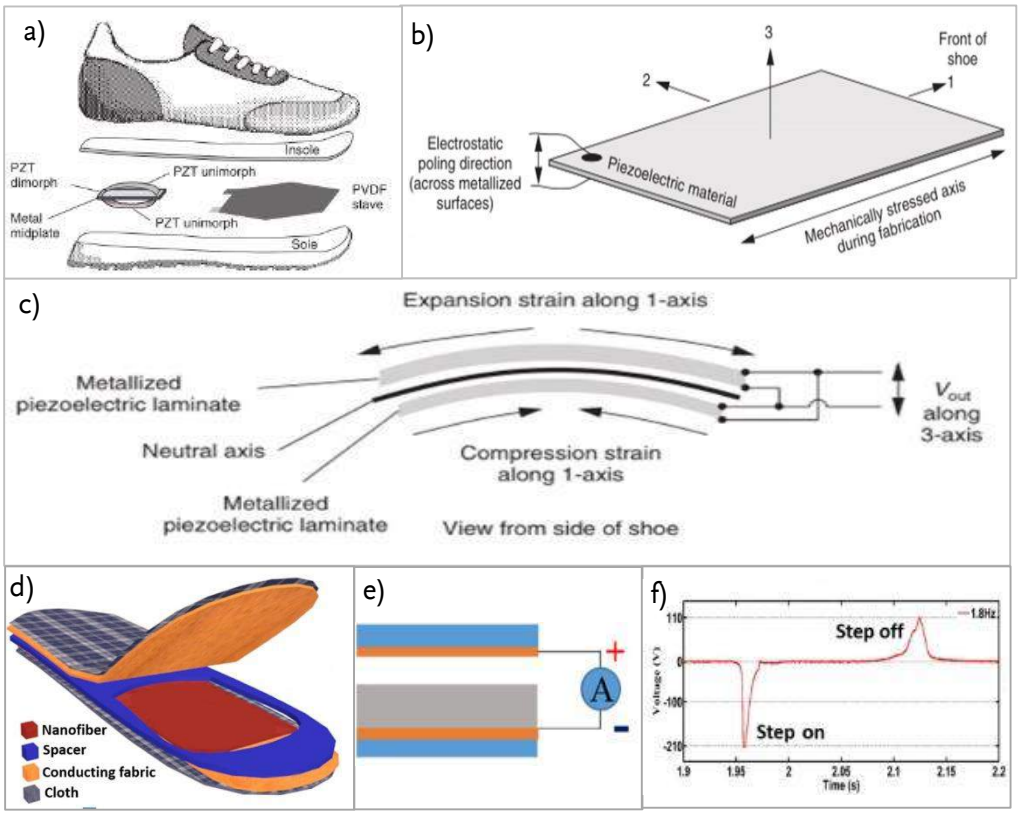


Fig. 32 – **a)** The use of a PVDF stave for scavenging energy from walking; **b)** Conventional axis definition for a piezoelectric material; **c)** The use of the 3–1 mode in bending for harnessing the energy in the shoe sole [183]; **d)** PVDF fibers sandwiched between conducting electrodes for walking energy scavenging; **e)** Configuration of the layers and schematic of the electrical circuit used for electricity generation **f)** Measurements of changes in voltage with walking; D–e) adapted from[118].

Zeng et al. [191] also produced a PVDF and $NaNbO_3$ based nanogenerator (**Fig. 33**). It is made of knitted fabric electrodes which sandwich a piezoelectric nonwoven fabric of

$NaNbO_3$ NWs and PVDF composite nanofibers. It manages to survive 1 million compression cycles without failure and consistently produces 3.4 V and 4.4 mA of peak voltage and current at 1 Hz pace of cyclic compression tests and a pressure comparable to that generated by normal human walking.

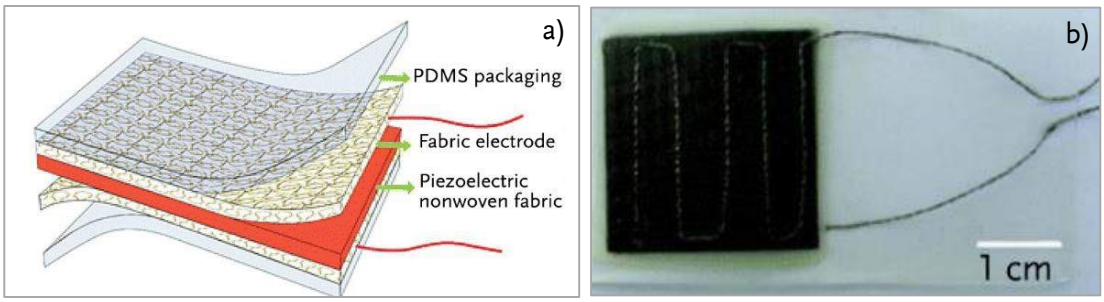


Fig. 33 – a) Schematic illustration of the structure of the electric nanogenerator; b) Photo of the fully package fabric ; Adapted from [191].

Yang et al. [192] also proposed a flexible hybrid energy cell for harvesting from solar, thermal and mechanical energy and tested the energy harvesting layers (**Fig. 34 b**). They created a nanogenerator by using PVDF which exhibits both the piezo and pyroelectric effect, for mechanical and thermal energy harvesting and a ZnO nanowire array-P3HT film solar cell for solar energy harnessing. Even though its only function is energy harvesting, due to its small thickness (the ZnO layer is just 2μm) it could potentially be integrated as a layer in a structural composite, such as the one in **Fig. 34 a**.

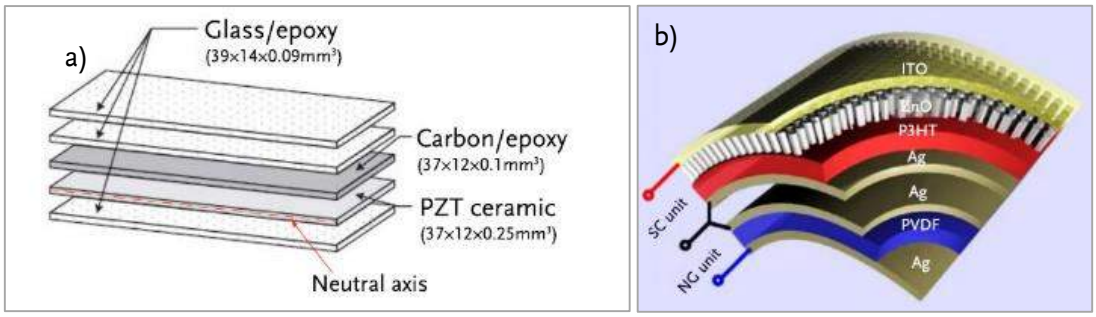


Fig. 34 – a) a piezocomposite for energy harvesting, adapted from [190]; b) Schematic of a flexible hybrid energy cell for harvesting from solar, thermal and mechanical energy adapted from [192].

Qi et al. [180] integrated flexible PZT piezoelectric buckled ribbons in a silicone-based substrate (Polydimethylsiloxane, PDMS), as shown in **Fig. 36 a**. This was accomplished by stretching a silicon-based organic polymer, adding the PZT with a nanoscale thickness ribbons, binding them and releasing the silicon. As it is released the PZT buckles allowing it to be stretched without breaking. Then a stretching action is able to generate and electric charge. Due to their small thickness and stretch ability they would be fit for integration in for example clothing material.

More recently new ways to use piezoelectric materials apart from the monolithic, *MFCs*, and hollow tubes have been appearing. ZnO has seen many uses in the form of nanowires. This shape is very interesting for it can allow an even greater integration with textiles up to type II. But even the most traditional piezoceramic, PZT, has been recently used in other shapes such as of ribbons [180] and nanofibers [193]. In fact nanofibers and nanowires are a new class of piezoelectric materials being heavily researched. Some recent reviews have been written on them [193, 194]. Several other examples are shown in **Fig. 36 b-f**.

Other curious recent applications is the harvesting of energy from dance-floors using piezoelectric materials though it still seems to be in the initial development stage [195], and a piezoelectric cable for an offshore power station, to harvest energy from sea waves (**Fig. 35**) [185]. The last one, for now it's much more expensive than photovoltaic or wind power (440M$/MWh vs 312$/MW and 611$/MW respectively) and has much less power-generation density than photovoltaic cells (521 μW/cm³ vs 15 000 μW/cm³).

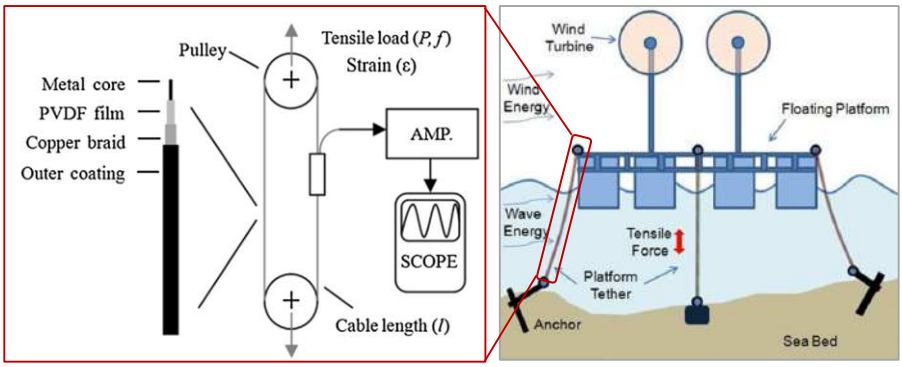


Fig. 35 – Piezoelectric cable for energy harvesting of sea waves' energy [185].

Now some challenges concerning energy harvesting using these MS are discussed. Most of the vibrational harvesters are designed to operate in the resonance frequency which limits the bandwidth they can be used. A specific case where this is an issue is on piezoelectric materials for vibration harvesting. Most are designed for the resonance mode and the half-power bandwidth, that is the bandwidth at which the output power is greater than half of its mid-band value, is often small. This is an issue because ambient vibrations have wildly varying frequencies from 1Hz of walking pace to 240Hz of an electric teapot [184].To overcome this, scientists are trying to convert the ambient vibration into a vibration at the resonance frequency of the material but this is hard to do [184].

Also, piezoelectric materials cannot hold large deformations, as most piezoelectric materials are usually brittle, and the power generation is still low at the μW and low mW range.

Then there is the fact that the most currently used piezoelectric material, PZT, has 60% m/m of Pb, which of course has harmful effects for the environment. The presence of

lead is so widespread that scientists devote their time to study lead-free piezoelectrics [196].

Then there are manufacturing challenges [197, 198]. Some low cost methods for the deposition of uniform films of piezoelectrics depend on the appropriate layers for proper nucleation and film growth and often result in very fragile piezoelectric films with properties far from the bulk material.

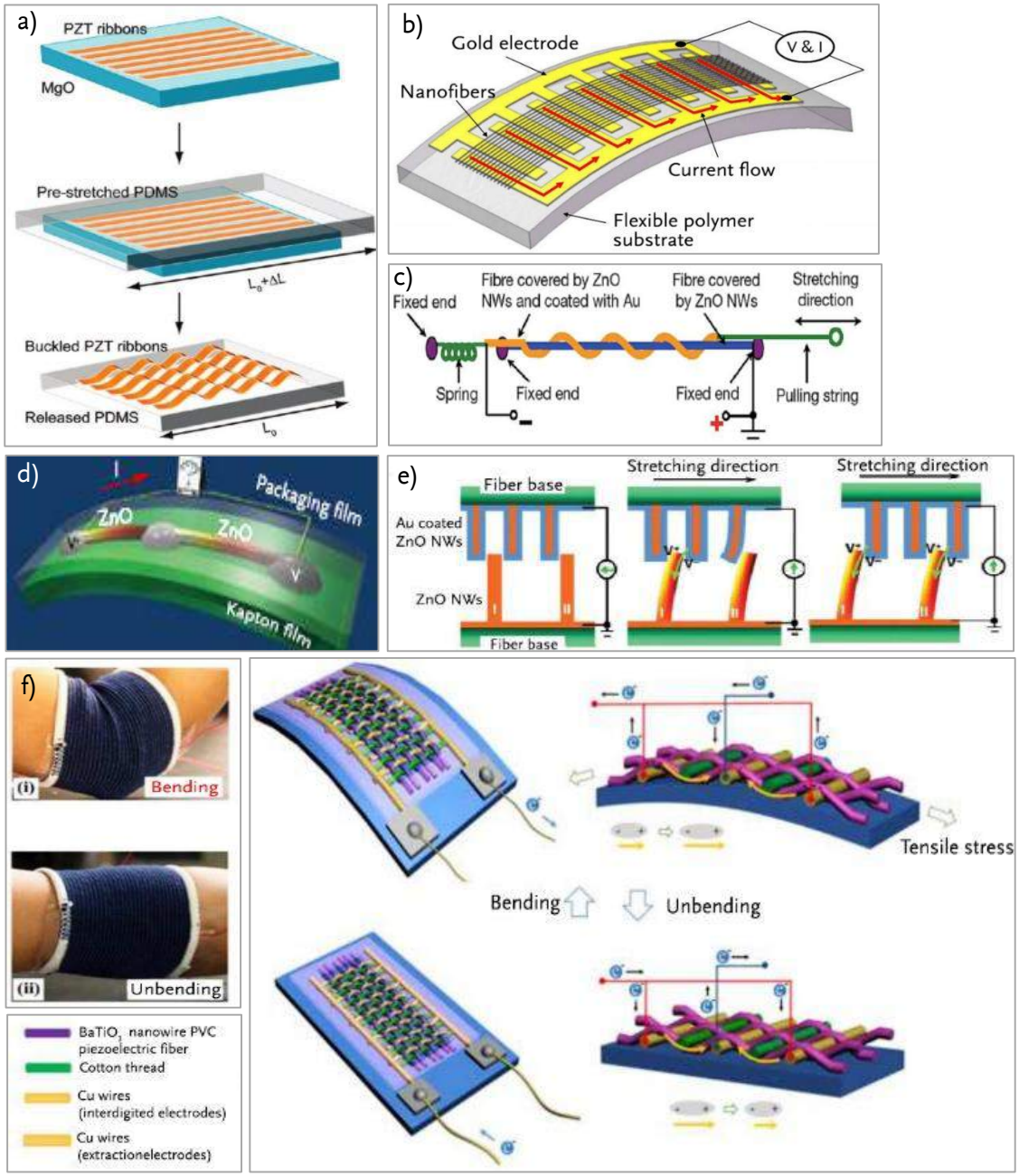


Fig. 36 – **a)** Formation of buckled piezoelectric PZT ribbons [180]; **b)** Diagram of a PVDF fiber structures and a comb-shape electrode on top of a flexible substrate [193]; **c)** Radially grown piezoelectric ZnO nanowires on polyamide fibers [170]; **d)** Illustration of series of ZnO fine wires, working as a generator, adapted from [170]; **e)** entangling flexible fibers with radially-grown ZnO nanowires [170];

f) A wearable nanogenerator based $BaTiO_3$ nanowire–PVC hybrid piezoelectric fibers, adapted from [120]

2.6 Shape Memory Materials

Shape memory materials (**SMMs**) are a type of SRMs that respond to thermal, pressure and magnetic field (**Fig. 37**). For example the SMMs that are responsive to thermal changes are thermo-responsive. When thermo-responsive **shape memory alloys** (**SMAs**) are heated above their transformation temperature, their martensitic crystal structure undergoes a change transforming into austenite and the materials return to their original shape.

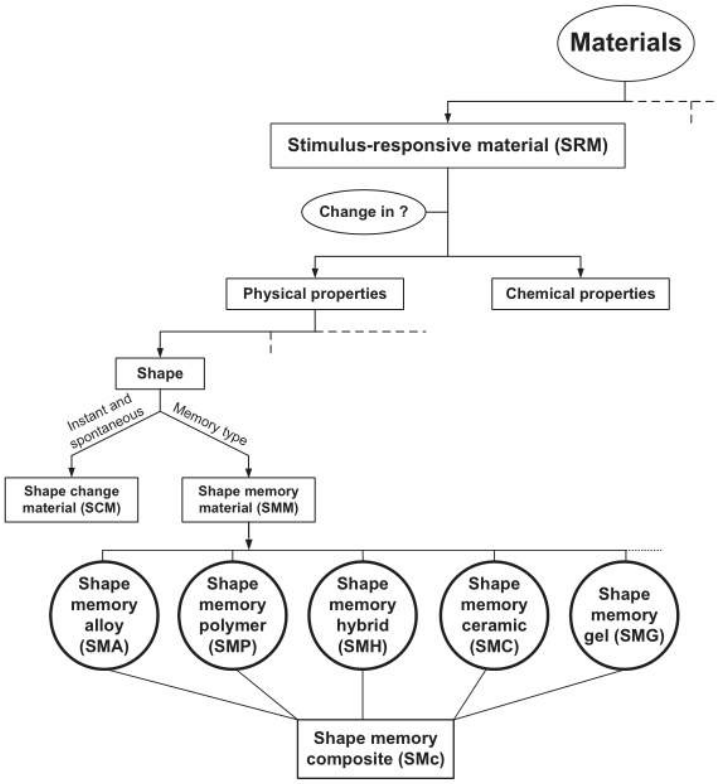


Fig. 37 – An overview of nomenclature related to SMM [199].

Nowadays the most used ones are SMAs and SMPs, though SMPs lead by far, as a literature survey reveals (**Fig. 38**).

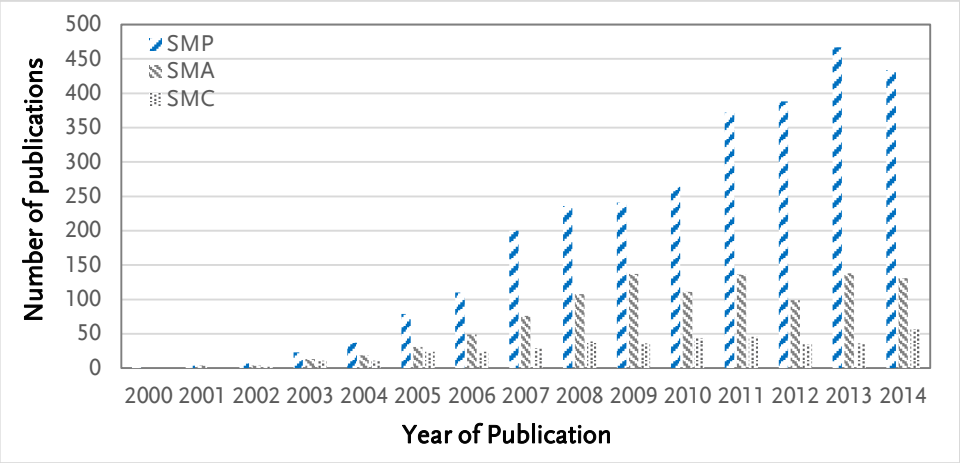


Fig. 38 – Number of journal articles related to SMPs, SMAs and SMCs, from EngineeringVillage.com at March 2015.

These materials have several applications, but the most related to multifunctional materials are for shape morphing structures.

Sun et al. [199] reviewed SMPs, SMAs and SMHs including applications and working mechanisms. We shall now divide the study between SMAs and SMPs focusing on the state-of-the-art related to multifunctionality.

SMA specific

SMAs are metallic alloys that can reversibly recover permanent strains when subject to a specific stimulus. This recovery occurs when the SMA goes back from the malleable martensite phase to the very stiff austenite.

The recovery can be induced:

- By specific temperature changes => thermo-responsive / thermally induced SMAs. The temperature at which the alloy changes to austenite depends on the composition, and it is very specific, so the material will always recover within 1-2ºC of that predetermined temperature. This transformation temperature generally falls on the 100-500ºC range. These are the most common SMAs.
- Magnetically => magneto-responsive / ferromagnetic SMA. These can actuate at higher frequencies than thermo-responsive SMAs (up to 1kHz) but are much more brittle and only able to operate at low temperatures [200].

SMAs can provide a very lightweight alternative to conventional actuators such as pneumatic, hydraulic or motor-based, since they are outstanding in terms of power/weight ratio over the other types of actuators (**Table 3**). Today a wide range of SMAs have been developed. Despite that, only NiTi-based, Cu-based and Fe-based are commercially important, in that order. NiTi is the most used SMA due to his good biocompatibility (for biomedical uses), excellent mechanical properties, good processability, good corrosion resistance, cyclic stability and wear resistance [201]. However thermally induced SMAs

suffer from a low operating cycle because of the time it takes to cool down and heat the material.

Table 3 – Comparison of actuator performance [199].

Actuator Type	Stress (MPa)	Strain (%)	Efficiency (%)	Bandwidth (Hz)	Work per Volume (J/cm^3)	Power per Volume (W/cm^3)
NiTi SMA	200	10	3	3	10	30
Piezoceramic	35	0.2	50	5000	0.035	175
Single crystal Piezoelectric	300	1.7	90	5800	2.55	15 000
Human Muscle	0.007-0.08	1-100	35	2-173	0.035	0.35
Hydraulic	20	50	80	4	5	20
Pneumatic	0.7	50	90	20	0.175	3.5

There are a few good recent references for a comprehensive review about the applications of SMAs. Among them Jani et al. [200] recently reviewed these materials, providing an overview about general applications, future opportunities and current challenges. Gupta et al. [20] also briefly introduced SMAs in the context of multifunctional and smart materials.

SMAs are used in morphing aerospace structures quite extensively [202]. Sofla et al. [203] reviewed aircraft wing morphing technologies while also developing a shape morphing aircraft wing using an antagonistically positioned SMAs material which flexes (**Fig. 39**).

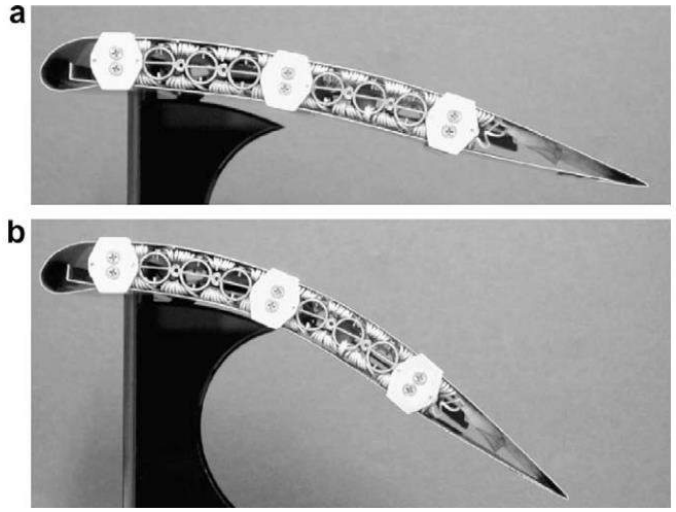


Fig. 39 – Bending achieved in a prototype aircraft wing by heating of SMA strips. a) Un-morphed and b) morphed[203].

In the trailing edges of some jet engines chevrons are used for noise reduction. Boeing developed a device known as variable geometry chevron to reduce take-off noise and increase cruise efficiency which is actuated by NiTi SMAs flexures [204] (**Fig. 40**).

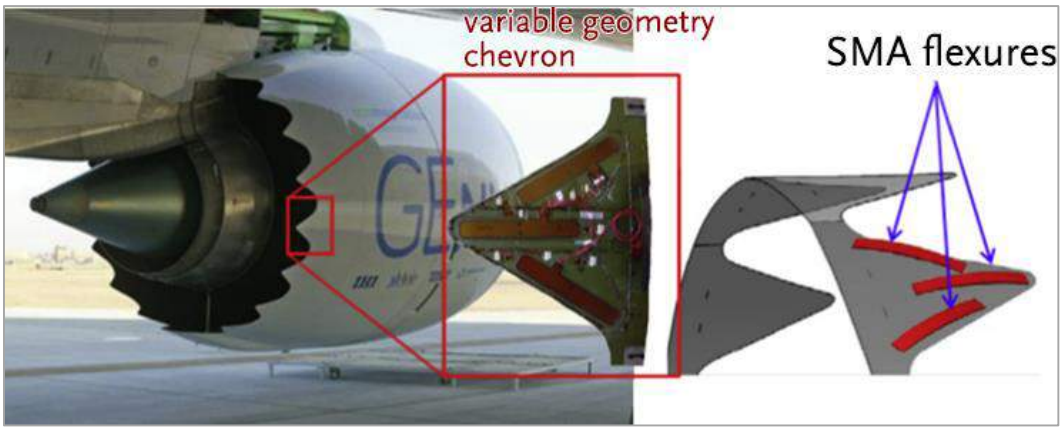


Fig. 40 – Variable geometry chevron developed by Boeing, adapted from [204].

There has been also some interest in creating biomimetic flapping wings actuated by SMA material. The material can be integrated in the structure of the wing as if they were muscles. One of such examples was a silicon wing with embedded NiTi strips developed by Sun et al. [199] (**Fig. 41**). The main issue is the low frequency of flapping, which is slightly less than 1Hz, mainly due to the large cooling time.

Despite the possibilities of these materials for aircraft morphing, for now the interest seems to be more geared towards using hydraulic actuators and strings since airplanes with seamless wings by Flexsys [205], NASA and Airforce Research Laboratory who are working on the project Environmentally Responsible Aviation (ERA) have successfully completed flying tests without any issues as of April of this year [206, 207].

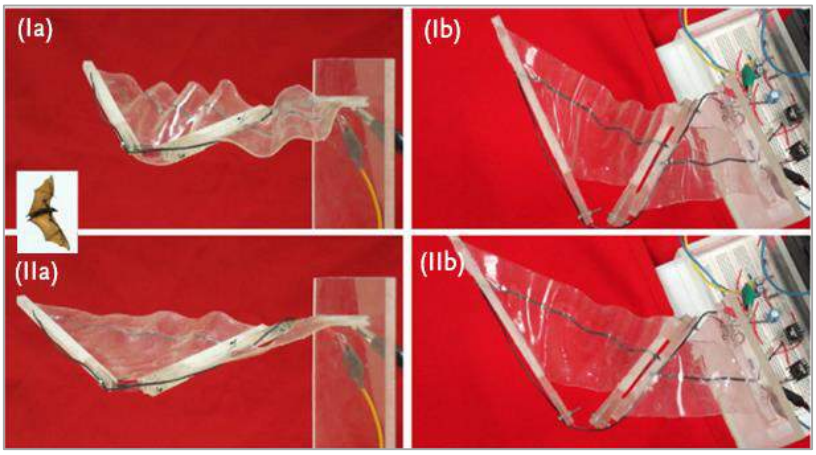


Fig. 41 –A bio-inspired silicon wing that opens and closes by joule heating the embedded NiTi SMA strip. Front a) and top b) views before I) and after II) heating, adapted from[199].

Coral et al. recently reviewed the state of the art of SMA-based muscle-like actuation in bio-inspired robots [208]. Some interesting solutions presented were a tentacle-like manipulator using SMA actuated hydrostats, the iTuna – a robotic fish with a SMA actuated backbone, and an earth worm-like robotic mimicking peristaltic movements, by using SMA wires that convert radial contraction into longitudinal lengthening.

In SMAs it is also possible to program multiple memory shapes, and this has seen a surge of interest in the recent years. This can be done using a new process known as multiple memory material technology [209] or by combining SMAs with other materials such as SMPs [210] resulting in a SMH with greater functionality, including sensing [211], magnetic refrigeration, active tissue scaffolding, energy harvesting [212] and self-healing capabilities [213, 214].

The self-healing functionality allowed by SMAs mainly consist on firstly reducing the gap of the fractured part by the shape memory effect, and then using some other mechanism to fill the much smaller space. Self-healing aided by SMA embedded materials has been reported by Huang, et al. [214] who produced a self-healing SMM made piece comprised of a SMA spring and a SMH tubular exterior. When broken, the spring was heated by the Joule effect making it return to its original compressed shape and compressing the two broken interfaces of the tubular SMH piece. That compressive force plus the heat from the Joule effect allowed the tubular piece to become once again with no visible fractures (**Fig. 42 a**, **b**). Eva et. al. [215] presented vast improvements in healing of an epoxy substrate with injected healing agent by including SMA wires, similar to what is shown in the same image **c**.

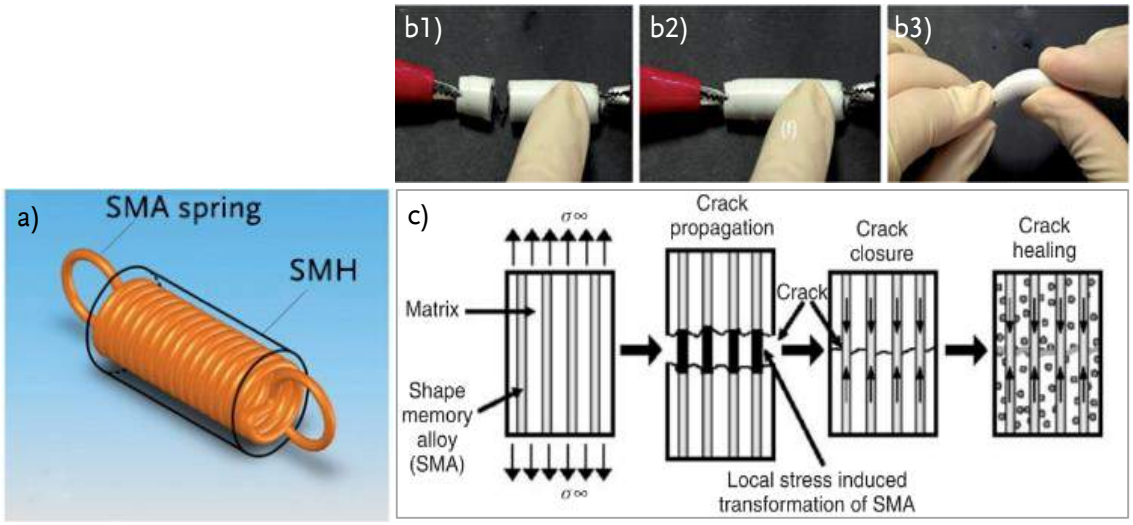


Fig. 42 – Self-healing of a SMH is shown. a) SMH with an embedded SMA spring inside; b1) pulling SMH till fracture; b2) joule heating SMA coil for self-healing; b3) healed specimen [214];c) [216].

A novel multifunctional material design was also presented by Pinto et al. [211] consisting of SMA wires embedded within traditional CFRP composites. The composite ought to have increased mechanical properties compared to regular CFRP composites, and also takes advantage of its electrothermal properties by using it as a sensor for self-monitoring and to serve as an embedded ice protection system for aerostructures.

It is also possible to combine SMAs with other materials. For example Sato et al. [217] succeeded in creating a fiber shaped quadruple functional material by depositing PZT

on NiTi, exhibiting the resulting material shape-memory effect, super-elasticity effect, piezoelectric effect, and pyroelectric effect.

SMP specific

Comparatively to SMAs, SMPs have many important advantages such as lower cost, density and easier processing, among others (**Table 4**). For these reasons many researchers are now turning to SMPs and trying to achieve their full potential.

Table 4 – Comparison between SMAs and SMPs [218–220]

(average values)	***SMP***	***SMA***
Cost	20 €/kg	500 €/kg
Density	0.9-1.25 g/cm³	6-8 g/cm³
Shape recoverability	up to 500%	up to 8%
Processing	Easy (< 200ºC, low pressure)	Hard (> 1000ºC, high pressure)
Tailoring of transition temperature, stiffness, bio-degradability and functionally grading	Easy	Hard
Response time	measured in seconds	measured in miliseconds
Number of cycles	very low	high
Recovery stress (related to Young's Modulus)	4 - 10MPa	200 - 400 MPa
Strength	5 - 100 MPa	700 - 2000 MPa

Still, nowadays even though SMPs lead in terms of investigation, SMAs have currently more commercial applications. Some recent reviews of the state-of-the-art of SMPs have been published [220-223]. These reviews go over topics ranging from their synthesis, types and their characterization, possible blends with other materials and reinforcements, current and future applications and potential future directions in their improvement including integration into MFC. Most studies concerning SMPs are about the thermoplastics ones, which have relatively poor thermal and mechanical properties (e.g. temperature, moisture and chemical resistance), so they aren't able to meet many requirements for multifunctional structural materials. However, thermosets, as well as thermoplastic SMPs reinforced with CF and CNTs, and other fillers are in development and show promise [222, 224].

The SM effect in polymers can be induced:

- **By specific changes in temperature** (thermo-responsive/thermal-sensitive) – these are the most known SMPs. They are a class of polymers that are easily deformable at high temperatures (average of about 70ºC) retain their shape when cooled and return to their original (high temperature) shape when heated again. This recovery of a previous memorized shape in polymers occurs due to glass transition. This change in temperature can be obtained:
    - directly through heat transfer from a heat source through conduction, convection of radiation;

    - electrically – through embedding electrically conducting particles/fibers such as carbon fillers;
    - magnetically – through embedding of magnetic fillers such as iron/iron-oxide, nickel, or cobalt compounds;
    - electromagnetically – a combination of the above;
    - exposure in a solution/water – when exposed, their glass transition temperature lowers the triggering of the SME.
- **By exposure to light** – these SMPs have their SME independent from any temperature effect. Light of different wavelength ranges is used for the fixation of the temporary and the recovery of the permanent shape instead of changes in the material's temperature;

Instead of directly supplying a thermo-responsive polymer with a source of heat, the other option is to do it indirectly by embedding materials that convert other forms of energy to heat and then trigger the shape recovery mechanism with stimulus such as laser energy and magnetism, the latter needing the polymer to be filled with magnetic nanoparticles [225]. This mixing of materials turns SMPs into truly multifunctional composites. These are some of the functions of SMPs which combine the mechanisms mentioned until now [226]:

- Actuation – a direct effect from the SME;
- Magnetic sensitivity – by using ferromagnetic fillers;
- Radiation sensitivity/opacity, namely RF, IR and UV – arise from the UV absorption properties of CNTs;
- Electrical sensitivity/conductivity – by using electrically conducting fillers such as CNTs and carbon black;
- Ability to change optical properties namely color and transparency (**Fig. 43**);
- Ability to change its water sensitivity/permeability – by changing the microstructure of the polymer [227, 228];
- High thermal conductivity – by using thermally conducting fillers as CNTs;
- Self-healing [229, 230];
- With magnetic interference shielding – allowed by reinforcement with MWCNTs [231];

In regards to actuation, electrical actuation has been studied [232, 233]. Liu et al. [233] studied different mechanisms to make it possible such as filling the SMP with conductive fillers as CNTs, electromagnetic fillers, adding magnetic particles such as Ni chains and adding hybrid fibers as micro-carbon powder and carbon black.

SMPs can also be combined with SMAs. For example, Ghost et al. [234] have shown how to combine SMAs and SMPs to form a smart material system, including a SMP with varying stiffness due to the variation of its glass transition temperature.

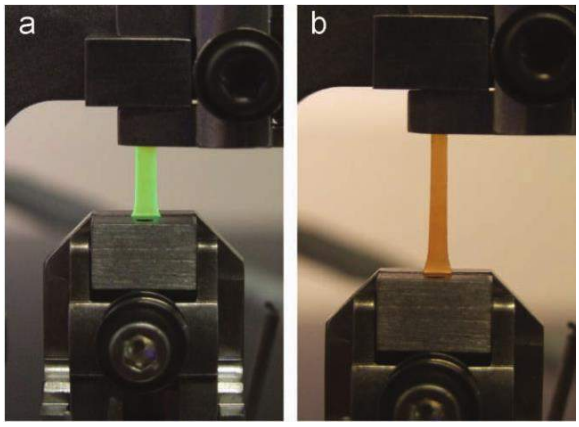


Fig. 43 – Change in color of a poly(cyclooctene) during deformation [235].

Like SMAs, SMPs also find applications in aerospace. The aerodynamic performance of aircrafts is designed for specific flight conditions, e.g. cruise for long range airliners, meaning that whenever the plane is not on the condition it was optimized for, efficiency is going to drop. For this reason there is great interest in expanding the optimal flight conditions, which could be obtained through morphing parts of the aircraft giving it the ability to change its geometry during flight. There are several attempts at implementing the concept of morphing wings [236]. Two examples concerning the use of SMPs as the actuation mechanism are shown in (**Fig. 44 a-b**).

Due to their shape morphing ability, SMPs are also being studied for use in deployable structures [237]. The main advantage of using SMPs for space applications is that it could greatly reduce the volume, weight, and cost of the structure compared with traditional self-deploying techniques. For example Keller et al. [238] have developed a deployable radio frequency reflector comprised of SMP-based composites claiming it is much more mechanically simpler and lighter than its conventional competitors (**Fig. 44 c-d**).

One of the most recent results of scientist searching for simple, cheap and light self-deployable structures is the development of cold hibernated elastic memory technology, which uses SMPs in open-cell foam structures or sandwich structures made of SMP foam cores and polymeric laminated-composite skins. The deployment occurs due to the SME and the foam's elastic recovery. This technology has found many space applications such as antennas, habitat structures, thermal shields, soft-landers and nanorover wheels (**Fig. 45**) [239].

Healable composite systems for primary load-bearing aircraft components have also been developed. Cornerstone Research Group Inc. [240] for example created a composite made of piezoelectric materials for SHM and SMPs for thermal activation. When damaged, the SHM system will locate and assess the severity of the damage ordering the heating of the SMP at the damaged location, and its shape recovery will partially heal the damage. This composite system was able to recover approximately 80% of its flexural strength upon bending test.

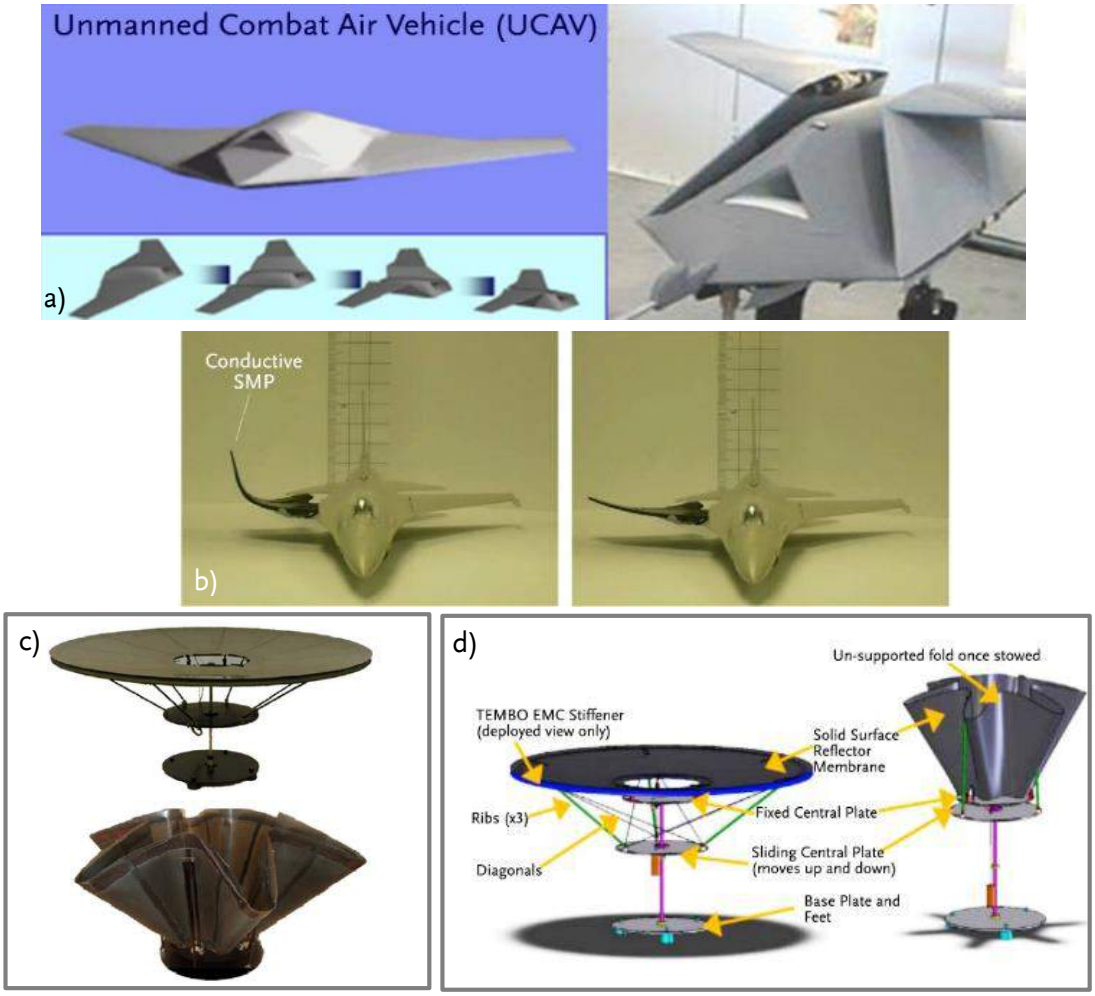


Fig. 44 – SMPs application in aerospace, so far mainly for actuation: **a)** Prototype of a morphing wing unmanned combat air vehicle by Lockheed Martin[222]; **b)** Conductive SMP for morphing wing, adapted from [239]; **c)** A SMP composite reflector in its pre-deformed (up) and recovered (down) shape; **d)** illustration of the structure of the reflector [238].

There are still a few challenges for SMA/Ps that are in need of being addressed. Herein I name a few:

- Low actuation frequency – the need to heat and cool down, especially the cool down process is slower because either it is due to passive cooling – slower – or active cooling – faster but increases complexity, costs and weight;
- Low energy efficiency: only about 8-17% of the heat energy received is transferred into work (Nitinol, NiTi - [241]);
- Low controllability – hard to control exactly the materials final temperature, hence it may overheat causing a significant reduction in fatigue life;
- More difficult to manufacture and machine when compared for instance with steel and aluminum and more expensive [20, 242];
- Low recovery force due to low recovery strength – SMPs only manage a few MPa while SMA can go over 10 MPa;
- Increase the number of operations of SMPs – currently they are only capable of a one-time operation, and so are not appropriate for use in cyclic actuations.

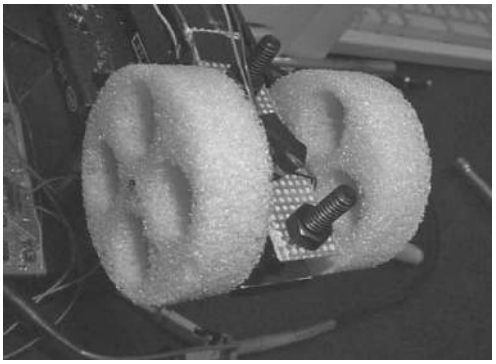


Fig. 45 – Self-deployable mini-rover wheels made using cold hibernated elastic memory technology [239].

Many of these problems are already being dealt with. The lack of strength of SMPs is being addressed with the reinforcement of fillers, namely CNT and CNF, nanoclays, SiC particles, carbon black, among others [220]. The problem of low fatigue life and reproducibility might soon become solved, as Chluba et al. [243] reported on the addition of copper impurities to NiTi SMA resulting in a ultra-low fatigue SMA that was able to withstand 1 million shape recoveries. Some of the other challenges developments are mentioned in a review of the progress towards overcoming the SMPs challenges by Rousseau [219].

2.7 Other

Apart from the large groups of materials mentioned until now – carbon based nano materials, FGMs, piezoelectric and SMMs – there are several other very interesting material systems that don't fit into a neat large group such as the ones mentioned. This subchapter is for those.

Aptamer based

A promising recent area of research is seeking to advance materials that use the presence of targeted molecules as a stimulus to trigger further changes to the system. These hybrid materials integrate a molecular recognition probe within that is specific to the molecules to which they are to respond to. The possible probes include antibodies, molecularly imprinted polymers and aptamer technology. A paper from Mastronardi et al. focused on the latter, based on the premise by earlier researchers that these are the most compatible for integration, which for now seems restricted to laboratories, with smart materials [244].

Carbon Fiber Reinforced Composites for Energy Storage and Sensing

The idea of adding energy storage function to high performance structural materials has been gaining increased attention. Carbon fiber reinforced composites are one of the candidates for structural batteries both type I (layered CF/epoxy-battery) and II (integration of energy storage material within the composite).

An initial application was for unmanned aircraft vehicles such as the DARPA Wasp micro air vehicle [245], which used a polymer Li-ion battery layered on top of the carbon-epoxy wing, managing to achieve a record-setting flight time (when compared to unifunctional designs) (**Fig. 46**).



Fig. 46 – The DARPA Wasp Micro Air Vehicle. The silver area has the embedded Li-ion battery in the wing structure [245].

Due to the resurgence of interest in electric cars in recent years, so has the interest in better batteries. Eric Jacques, a researcher in vehicle and aerospace engineering at KTH, has mentioned how carbon fiber can fill two functions in an electric car: as a lightweight composite reinforcement material for the car's body, and as an active electrode in lithium ion batteries. He says carbon fiber offers a viable alternative to graphite. Lithium can be inserted into the carbon fiber microstructure and the carbon fiber acts as a good conductor [246].

The weight of the battery is one of the largest obstacles to overcome for electric and hybrid vehicles. As we will see, a structural battery could massively increase the overall system's efficiency. Fortunately this technology is already alive and improving. Drayson Racing Technologies and Lola first presented the Lola Drayson B12/69EV, an electric racing car that uses a composite structural battery to aid the main battery for powering (**Fig. 47**) [247].

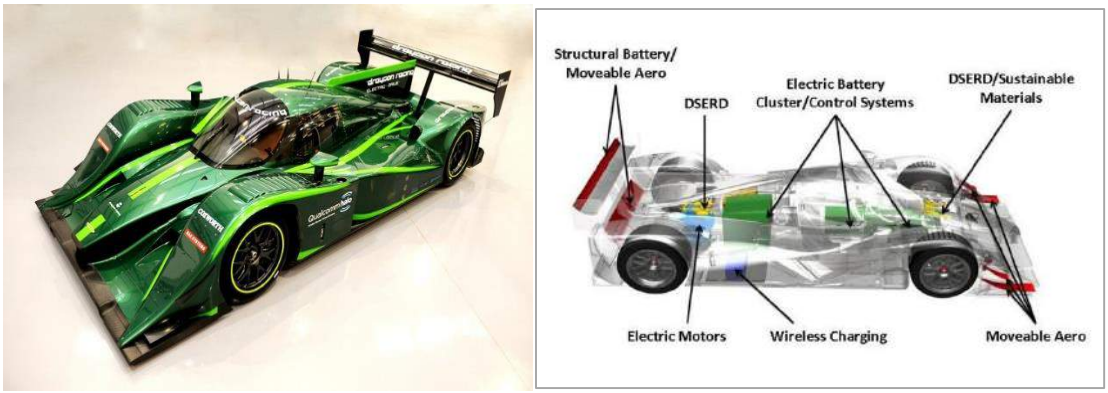


Fig. 47 – Lola Drayson B12/69EV electric racing car with nickel–based and CF structural–batteries. [248]

Even though the way the composite was achieved in the Lola Drayson, and many others, are hidden inside the R&D of industries, other researches might give a hint due to research of their own. Pereira [249] obtained a CF/epoxy with energy storage function by embedding thin film lithium energy cells within the CF layers. The strength and stiffness of the carbon/epoxy laminate was not significantly changed, and there was no abnormalities in the energy cells' charging and discharging processes when the composite was mechanically loaded to up to 50% of its ultimate tensile strength.

Since 2010 Volvo, together with Imperial College of London and nine other European companies and institutes, have been developing body panels for cars that store energy (**Fig. 48**) [250]. In an interview it is shown the charging of a simple sheet of a carbon fiber multifunctional composite being charged and subsequently being used to illuminate a light. Conservative estimations on weight savings approach 15%. Moreover, there would be much less wiring since energy could be withdrawn from several sources on the car that are closer to the device. The materials consist of carbon fibers, nanostructured capacitors and super capacitors.

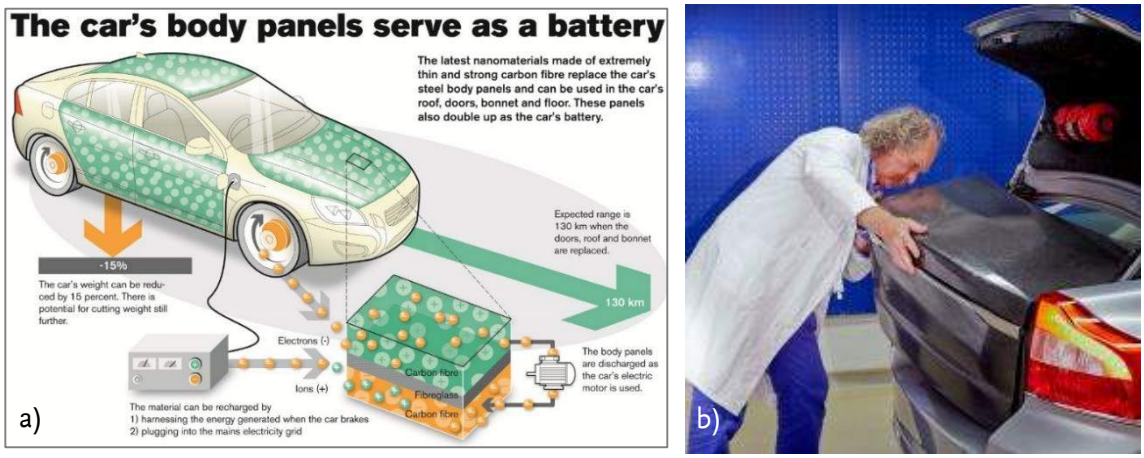


Fig. 48 – a) A diagram explaining the concept for structural vehicle batteries being designed by Volvo in partnership with Imperial College of London [250]; b) One of the developers showing how a structure–battery panel would fit like a normal panel [251].

As for the batteries' electrolyte, Snyder et al. [252] studied different formulations in order to obtain structural batteries in the range between highly conductive but structurally weak to the inverse. Unfortunately they found that the Young's modulus and the electrical conductivity were inversely related.

One of the difficulties pointed out is in finding custom Li-ion cells because there are very few manufacturers that are willing to making them. This is because the production of batteries is typically for large series (thousands to millions) meaning that small (10-100) custom lots can be prohibitively costly as they need to be manually made. In a study about the design and application of structural batteries Thomas et al. complain how just the custom cells they had to purchase cost several thousands of dollars per unit [245].

Another issue is that structural-batteries need to be longer lasting than conventional batteries. One can't just replace an aircraft wing or a car aileron after 2-3 years of use, like it's done with mobile phone batteries. They should last for decades. This requires synergy in the performance life between the structural material and the energy device. This is an advantage for supercapacitors because even though they store ten times less energy than current lithium-ion batteries, they can last a thousand times longer, meaning they are better suited for structural applications.

There are those who also focus on giving CFRP capacitor functionality. An example of a structural capacitor was the one developed by Luo and Chung [253] with a capacitance of 1.2μF/m^2 which consisted of a carbon/epoxy laminate with a paper in-between to reduce through-the-thickness conductivity. Unfortunately the capacitor was not mechanically tested.

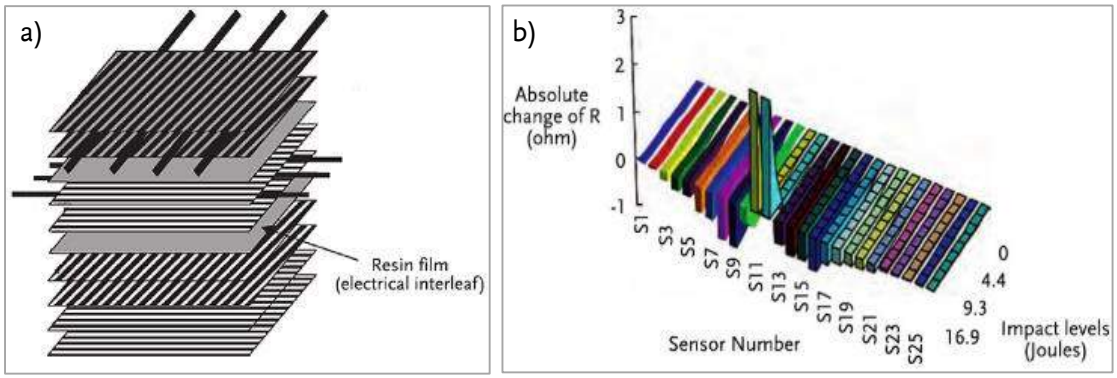


Fig. 49 – a) Illustration of the self-sensing CFRP, the layup orientations and the presence of an electrical interleaf to isolate sensing plies; b) Resistance change across mounted sensors denoting damage in fibers corresponding to sensors 3-21.Adapted from [254].

Scientists have been trying to improve the energy storage capabilities of supercapacitors, but one of the biggest problems in designing load-bearing supercapacitors is preventing them from delaminating [255].

In terms of sensing, the ability to detect and locate damage on a CFRP has also been accomplished by Hou et al. [254] by measuring electrical conductivity along the fibers.

In places where fibers are fractured, resistance increased, whereas in places where inter-fiber contacts were disrupted, it decreased (**Fig. 49**).

Cement-based and conducting elastomer

Ubertini et al. [256] developed two novel sensors for SHM of civil structures, one that uses a self-sensing cement paste that can be applied over large linear concrete structures segments or embedded in them, allowing their monitoring while contributing to load bearing. The other is a soft-elastomeric capacitor that can be applied over large surface areas, providing the structure an external sensing skin.

Commercial 3D Printing Materials

By using VeroBlack and TangoPlus, two 3D printing optimized polymers, Guttag et al. [257] created a composite with dynamically controllable surface texture (**Fig. 50**).

The 3D printed composite is composed of a soft elastomeric matrix (TangoPlus) which has embedded stiff particles (VeroBlack) which, upon the application of external stimuli, is able to conform its surface to have several kinds of features.

According to the researchers the technique also allows for directionality to occur, so for example, they could create a surface that is smooth in one direction but rough in the opposite, and also since it also relies on the geometry of the particles it is scalable to any size.

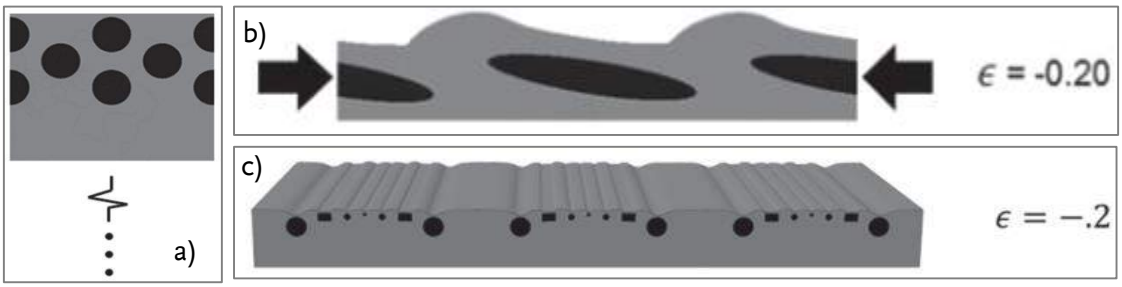


Fig. 50 – a) Basic setup of the composite – black circles: VeroBlack stiff particles, grey matrix: TangoPlus elastomer; b) at a certain compressive strain the particles rotate resulting in anisotropy of the texture; c) Simulation used to observe the effect of using inhomogeneous with variable shape particles [257].

Copper Nano-ink

A laminate for simultaneous energy harvesting and storing was developed by Kim et al. [258] by using a printed by inkjet at a nano-scale copper circuit on a polymer film to connect a thin film solar module to a thin film lithium-ion battery. It resulted in a single film which was then embedded and co-cured within carbon/epoxy prepreg layers to fabricate an energy harvesting and storage composite.

Foams

There are plenty of foams out there but I'd like to mention two I found appropriate for the topic of MFMS. The first one are syntactic foams, which are a class of particulate

composites where materials are filled with hollow particles. This way instead of the porosity simply consisting of gas, each porosity is encapsulated in a stiff and strong shell, resulting in foams with significantly higher modulus and strength but similar density. They are still in their infancy, but I find this concept promising since the presence of the hollow particles not only increases specific properties but could also add new functionalities to the material they fill.

The second one is Aerographite: A 3D network of porous carbon tubes with a density of just 2kg/m^3, making it the lightest material currently known, electrically conductive and with a capacity to be compressed to 95% of its volume returning to the original volume without any damage. Due to its hierarchical structure, and the resulting very low density, it has outstanding specific properties such as stiffness and tensile strength. Its morphology is also susceptible to be significantly changed concerning aspect ratios, diameters of the tubes, and the structure of the surface.

It was produced by using a sacrificial template made of ZnO that was put into a carbon enriched atmosphere. Heating it to a certain temperature then introducing H_2 which reacts with the ZnO resulting in steam and Zn gas leaving the light carbon foam Aerographite behind [259].

Glass Fiber

A solution that improves impact resistance along with sound/vibration damping while also being designed for future sensor and wire integration was proposed by Vaidya et al. [162]. The proposed solution consists of a sandwich structure in which the woven E-glass face sheets are connected to the vertical woven E-glass piles and to the foam core.

Bai et al. [260] have also demonstrated the viability of creating self-luminous glass fiber reinforced polymer composites by using a translucent resin mixed with self-luminous powders in the matrix without any loss of load-bearing capacity of the composite.

Kevlar Composites for CLAS

The development of composites with integrated broad band radio frequency antenna – also called conformal load bearing antenna structure (CLAS) – for the use on the skin of fighter aircrafts [261-263] is the scope of the program named Smart Skin Structure Technology Demonstration (S3 TD) which is sponsored by the US Air Force's. Yao et al. attempted to achieve full integration by developing a microstrip antenna incorporated in a 3D orthogonal woven composite structure of Kevlar 129/vinyl ester composite [264].

Kevlar Fibers Coated With Polymers

Lee et al. [265] developed a fiber-based pressure sensor with unprecedented sensitivity, excellent durability and quick response, comprised of highly conductive fibers coated with dielectric rubber materials (**Fig. 51**). The conductive fibers were fabricated by coating poly(styrene-block-butadienstyrene) (SBS) polymer on the surface of poly(p-phenyl-

eneterephthalamide) (Kevlar) fiber, followed by converting silver (Ag) ions into Ag nanoparticles directly in the SBS polymer. It changes its capacitance when subject to transverse pressure. To prove its feasibility, the authors embedded the fibers along with data transmission in gloves and used them to control drones with finger movements.

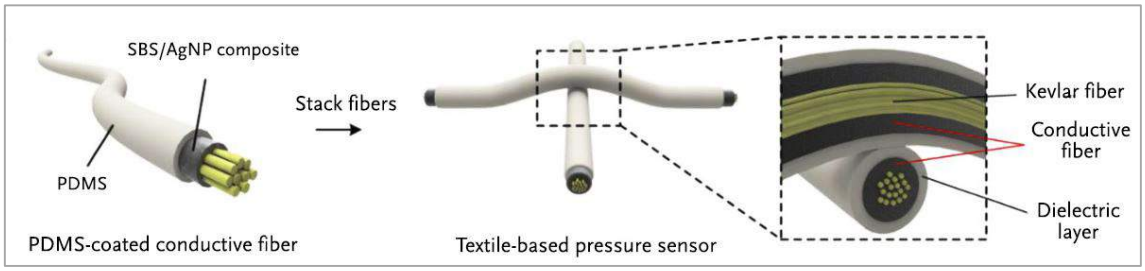


Fig. 51 – A hybrid textile based pressure sensor [265].

NiF_2 on PET

Yang et al. [266] created flexible (holding 76% of its original energetic capacity after 10 000 discharge cycles and 1 000 bending cycles) super-thin (0.25mm) supercapacitor that can behave like a battery, that is, it can charge and discharge slowly (**Fig. 52**). This technology could be used not only in wearable electronics but also in conjunction with shape changing materials.

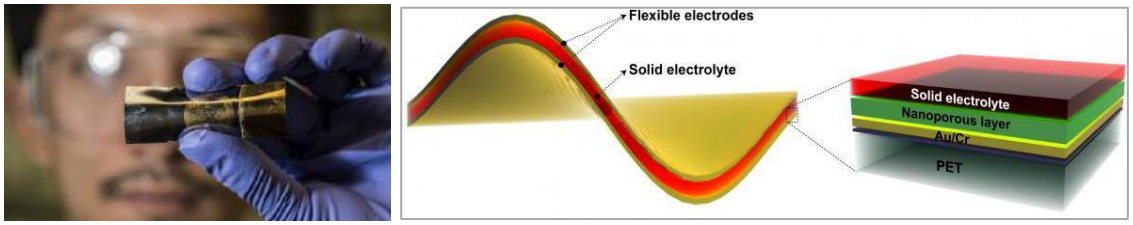


Fig. 52 – A flexible ultra-thin supercapacitor developed by Yang et al. [266, 267].

Materials with Sandwich Structures for Increased Thermal Properties

As proposed by Wirtz et al. [268] a sandwich structure can be used as a thermal energy storing device along with a structural function for the temperature control system of an electronics module. Heat is stored on the phase changed material's latent heat. The mechanical behavior of such structure was also described and it was found to have a good performance-to-weight ratio. Other projects on this subject include the sandwich structural-heat pipe developed by Queheillalt et al. [269] and the multifunctional sandwich panels for space satellites by Ozaki et al. [270]. Through-the-thickness and in-plane thermal conductivities were improved in sandwich panels by using a carbon foam core along with face sheets made of carbon fiber composite by Silverman [271] for the use in lightweight spacecraft thermal radiators.

Metallic–Intermetallic Laminate Composites

Metallic-intermetallic laminate (MIL) composites are composites made of a combination of metal and intermetallic laminates. The composition, physical, and mechanical properties of the MIL composites can be tailored by varying the individual foil compositions, thickness, and layup sequence. The processing is also relatively easy. In the case of one well known MIL, due to its high specific properties, Ti-Al_3Ti, the processing temps are below 700ºC and the pressures below 4MPa without the need for any special atmosphere. They have mainly potential for type I multifunctionality.

Since these composites are obtained by initially ductile metallic foils, this allows easy shaping of the layers allowing non-planar structures such as tubes, shafts and rods to be formed. Since they can also be machined, we can obtain other more complex structures as well as cavities for the incorporation of other functionalities such as passive damping or sensors [272]. Other functionalities, apart from structural, are also ballistic protection and thermal management (thermal energy storing or conduction).

Fig. 53 a shows a typical structure of a Ti-Al_3Ti MIL, and **b** the introduction of cavities in the intermetallic layer for vibration damping functionality. Their size, distribution and location can be designed and produced for each individual layer, and can also be filled with granular materials to serve as particle dampers. **Fig. 53 c** shows a MIL of Nitinol and Ni-Ti Aluminide with embedded tubes that can absorb energy that could return to their original shape through heating.

Other functionalities could be obtained through the embedding of other materials or devices in the cavities, mainly in the intermetallic layers.

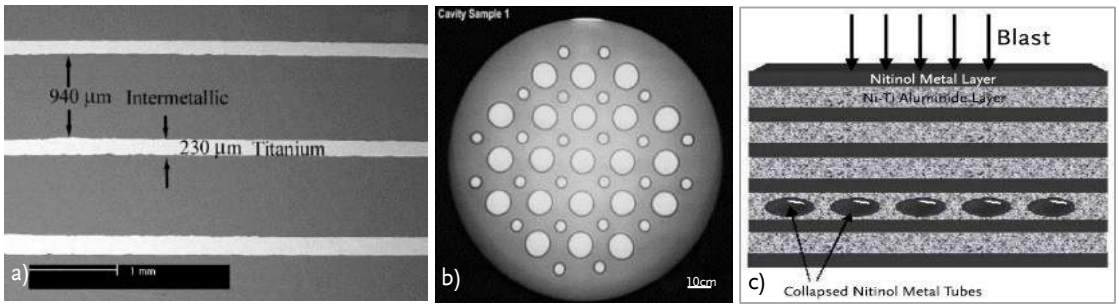


Fig. 53 – a) typical structure of Ti–Al_3Ti MIL; b) X-ray fluoroscope image of through-thickness cavities created within the intermetallic layer of a Ti–Al_3Ti MIL composite for vibration damping; c) embedded tubes within the intermetallic layers for energy absorption [272].

Polyaniline

Polyaniline (PANI) is an intrinsically conducting polymer (ICP) meaning it conducts electric current without needing electrically conducting fillers like other polymers do. ICPs are of interest because of their uses in batteries, antistatic shielding, anticorrosion coatings [273] chemical sensing [274] and environmental remediation [275]. Of all the

current ICPs known, PANI is currently the most promising because it is easy to synthesize, cheap and chemically stable [276, 277].

Porous Silicon

Westover et al. [255] demonstrated a multifunctional material capable of simultaneously store energy (energy density of 10Wh/kg) and withstand static (up to 300kPa) and dynamic mechanical stresses (up to 80G's). This new material is a supercapacitor that stores electricity by assembling electrically charged ions on the surface of a porous material, instead of storing it in potential chemical reactions the way conventional batteries do. The materials are nanoscale-porous electrodes of silicon coated with a protective ultrathin graphene-like layer of carbon. A polymer film acting as a reservoir of charged ions is sandwiched between the two electrodes. By pressing the electrodes together, the polymer is forced to penetrate into the tiny pores of the electrodes. After it cools down and solidifies it forms an extremely strong mechanical bond.

Silver–Silica–Silver Material System

Using a 3 layer Silver-Silica-Silver MS with high-resolution printed arrayed holes, Cheng et al. [278] created a plasmonic nanostructure that exhibits visible light color with low dependence on incidence angles and on the presence of a polymer layer on top, for protection purposes. By altering the holes' diameter, which they tested from 45nm to 75nm, and distance between each other they were able to control the displayed colors, which were pure and with high brightness (**Fig. 54**).

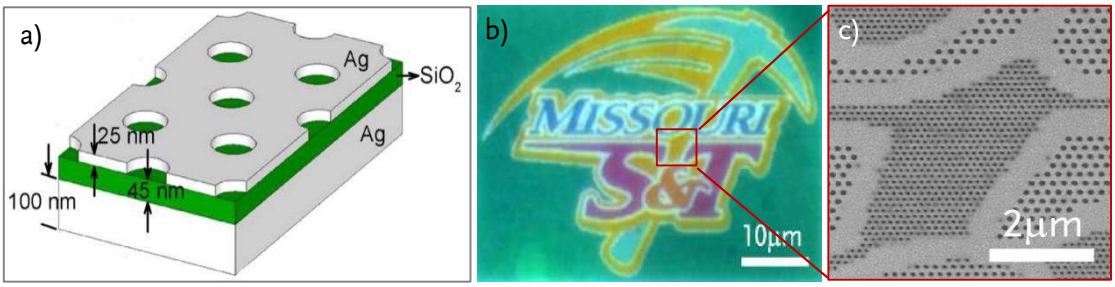


Fig. 54 – a) Illustration of the composition and structure of the plasmonic metasurface; b) Optical microscopic image of the plasmonic print; c) SEM micrograph of a detail of the fabricated pattern[278].

Zinc Oxide

Bagal et al. [279] developed a flexible (increased rupture strain of up to 51% of planar ZnO), electrically conductive and transparent ZnO-PDMS structure. It was created by using atomic layer deposition to deposit a ZnO layer on top of a photoresist which had been worked on using interference lithography to create nanoridges of various heights (**Fig. 55**).

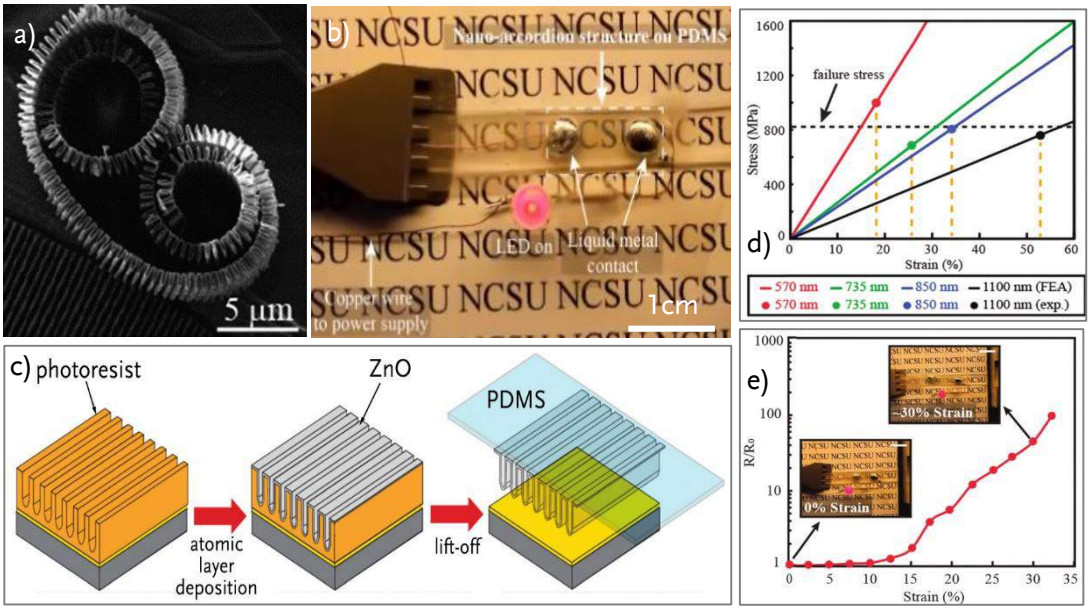


Fig. 55 – a) SEM micrograph of the ZnO nano-accordion; b) Test setup for mechanical and electrical characterization; c) Process of fabrication of the structure; d) Part of the mechanical characterization. The size values represent the height of the ridges; e) Part of the electrical characterization revealing changing electrical resistivity with strain. Adapted from [279].

2.8 By functions

here are other materials or frameworks being developed which are made of several constituent materials or research that involves several materials, where the common factor is function. For these, a grouping by function makes more sense.

Energy related

In previous chapters structural energy storing composites were already mentioned. Here I present a few of the remaining that didn't fit in the other groups namely structural capacitors and autophagous composites.

A comparison of several structural capacitors focusing on their stiffness and energy density was made by O'Brien et al.[280] (**Fig. 56**). This comparison shows that regular capacitors have high energy density but poor stiffness and conventional structural composites have the opposite relationship. In this case it meant that none of the materials evaluated achieved the threshold – represented as a dashed line – for having a total efficiency at least as good as the unifunctional components separated, which would mean for the same load bearing capacity and energy storage density, the final component would weigh the same. That threshold seems to have been surpassed according to claims by Baechle et al. [281] who created dielectric capacitors of laminated glass-epoxy prepregs with metalized film electrodes.

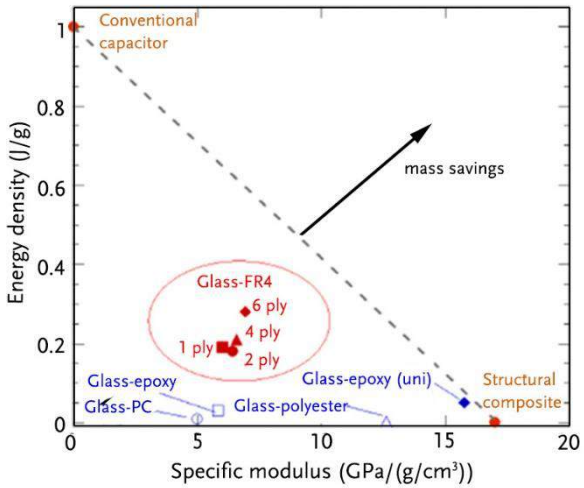


Fig. 56 – Comparison between structural capacitors. The dashed line represents the threshold above which the system's weight is less than combined weight of each of unifunctional subsystems. Adapted from [280].

As part of the DARPA Synthetic Multifunctional Materials Program, Neudeucker and Benson [282] have proposed a "PowerFiber" which consists of a structural and energy storing fiber whose concept can be used for several materials (**Fig. 57 a**). The same authors developed such a fiber based on SiC and carbon and Lithium (**Fig. 57 b**,**c**) which was able to store up to 0.8μAh at 1.5V for eight 150μm diameter 5cm long fibers.

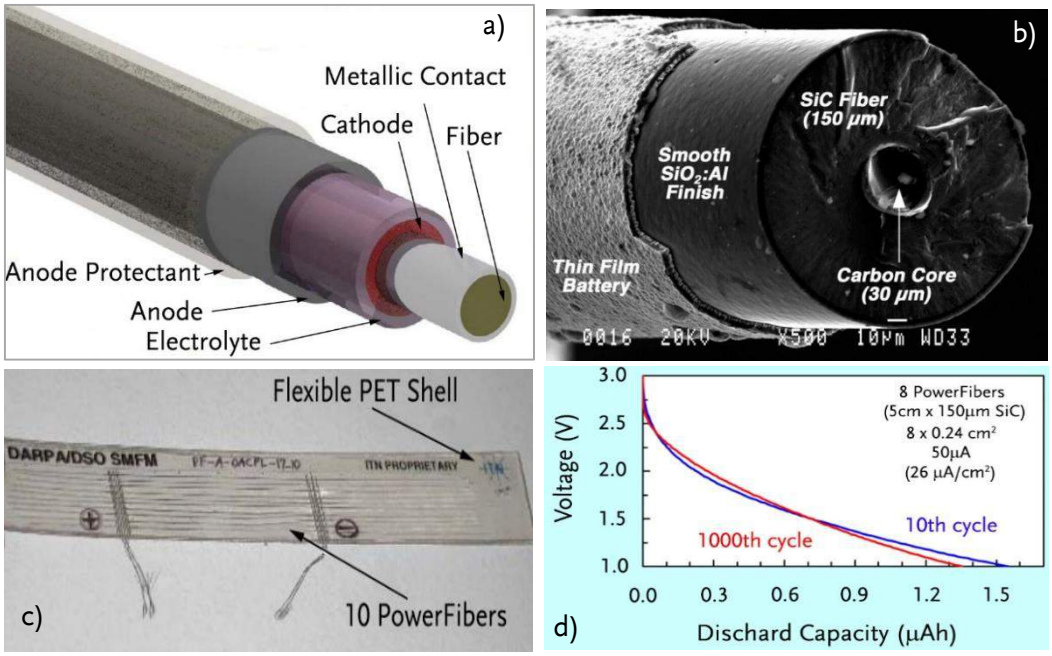


Fig. 57 – a) The structural and energy storing 'Power Fiber' b) SEM micrograph of a SiC 'Power Fiber' c) Photo of 'Power Fibers' embedded in a PET matrix ('Power Composite'); d) 'Power composite's' discharge capacity and voltage after 990 charging–discharing cycles; a–d) adapted from [282].

Batteries aren't made for structural purposes, but with the increasing in interest in structural batteries, the question of how Li-ion batteries behave when subject to loads has arisen. In his thesis [283], Hyoncheol Kim analyzed the effects of structural, thermal,

fabrication and kinetics effects on lithium-ion batteries for the purpose of their integration in structural-batteries where he said there had been low understanding of their effects on batteries due to the premise that they are to be kept in a stress free environment. Suabedissen, et al. [284] concluded that applying stress not only decreases batteries' capacity early on, but can also lead to its shorting.

Structural energy storage mediums, such as the ones that have been presented before, are a field of research where there is a great amount of funding going into. For example, ARPA-E in 2013 alone gave away $56M in funding for the development of electrical vehicles' storage [285, 286]. The U.S. Department of Energy's Advanced Research Project Agency for Energy is investing $8.7 million in research projects concerning integrating energy storage capabilities in structural materials [287]. It is to expect that great improvements to this area will quickly follow.

Finally there is another lowly researched area which concerns autophagous composites, that is, which can be consumed to generate electrical power after the part they constitute is no longer needed, for example in space propulsion systems after the fuel has been consumed [288]. An example of such a composite has been proposed by Joshi et al. [289] which consisted of thermoplastic matrix composites with incorporated oxidizers which demonstrated a significant energy output from directly burning the material.

Clothing

Clothing might not be something one thinks of when looking for MFMS, but some of them do have multifunctionality. With the improvements in nanofibers such as CNTs and TiO nanowires and new thin films such as graphene, the possibilities for innovation increase and so does funding, such as by the PROETEX European project for advanced e-texiles for firefighers [290].

Starting with the simpler ones, many raincoats are multifunctional structures with several layers each with a different purpose. An external waterproof rubber-like layer, an interior layer for comfort to skin contact including the ability to absorb moisture to maintain the skin dry, and an intermediate layer for thermal isolation.

More extreme cases of this include firefighters' clothes (**Fig. 58**). In those there's an outer shell generally consisting of woven fabrics and whose function is to provide flame (1), thermal (2) and mechanical resistance (3). Inside there's the moisture barrier made of breathable (4) moisture-resistant (5) film laminated to a substrate for stability. Then thermal liner which is composed of layers of flame-resistant and thermally-insulate non-woven fabrics that are attached to a woven facecloth for stability and strength, totaling 5 functions.

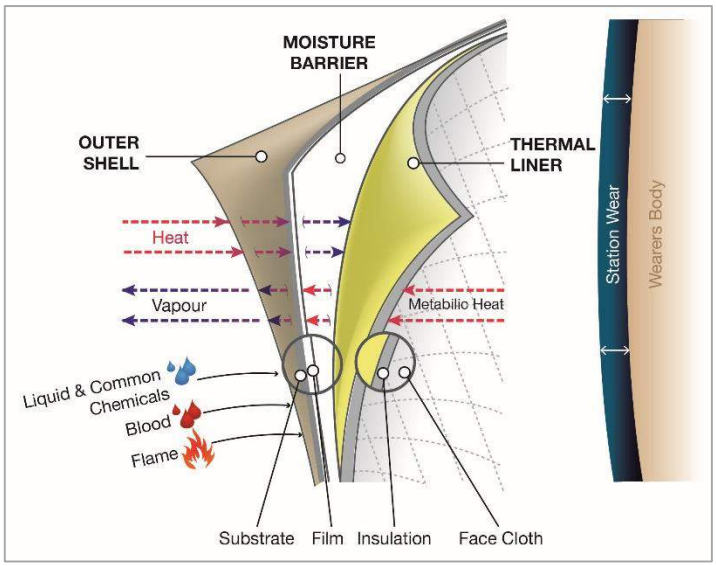


Fig. 58 –Typical layers of firefighting jacket [291].

Other wearable type I multifunctional structures have been presented on the chapters concerning piezoelectric and carbon-based nanocomposites. More recently there has been an increasing interest in a more integrated (type II) for wearable devices and clothes.

Liu and colleagues [292] produced a small solar cell with a multimaterial wire with MWCNTs enveloping it, to function as a power source with a 1.78% efficiency of energy conversion with no decrease after 1000 bending cycles. The MWCNT provides flexibility and mechanical strength and functions as the anode and the Ti coated wire absorbs solar energy and functions as the cathode (**Fig. 59 a-c**).

On the other hand, energy storage fibers for wearable devices/clothing are also being developed such as a cable-like supercapacitor made of SWCNTs coated cotton thread (**Fig. 59 d**) [293], and an energy storing multimaterial fiber composed of CNT-Si/CNT yarns as the anode, and CNT/(Lithium Manganate (LMO)) yarns as the cathode (**Fig. 59 f-h**). Other examples and the state-of-the-art of wearable applications can be seen at the recent review by Zeng et al. [294].

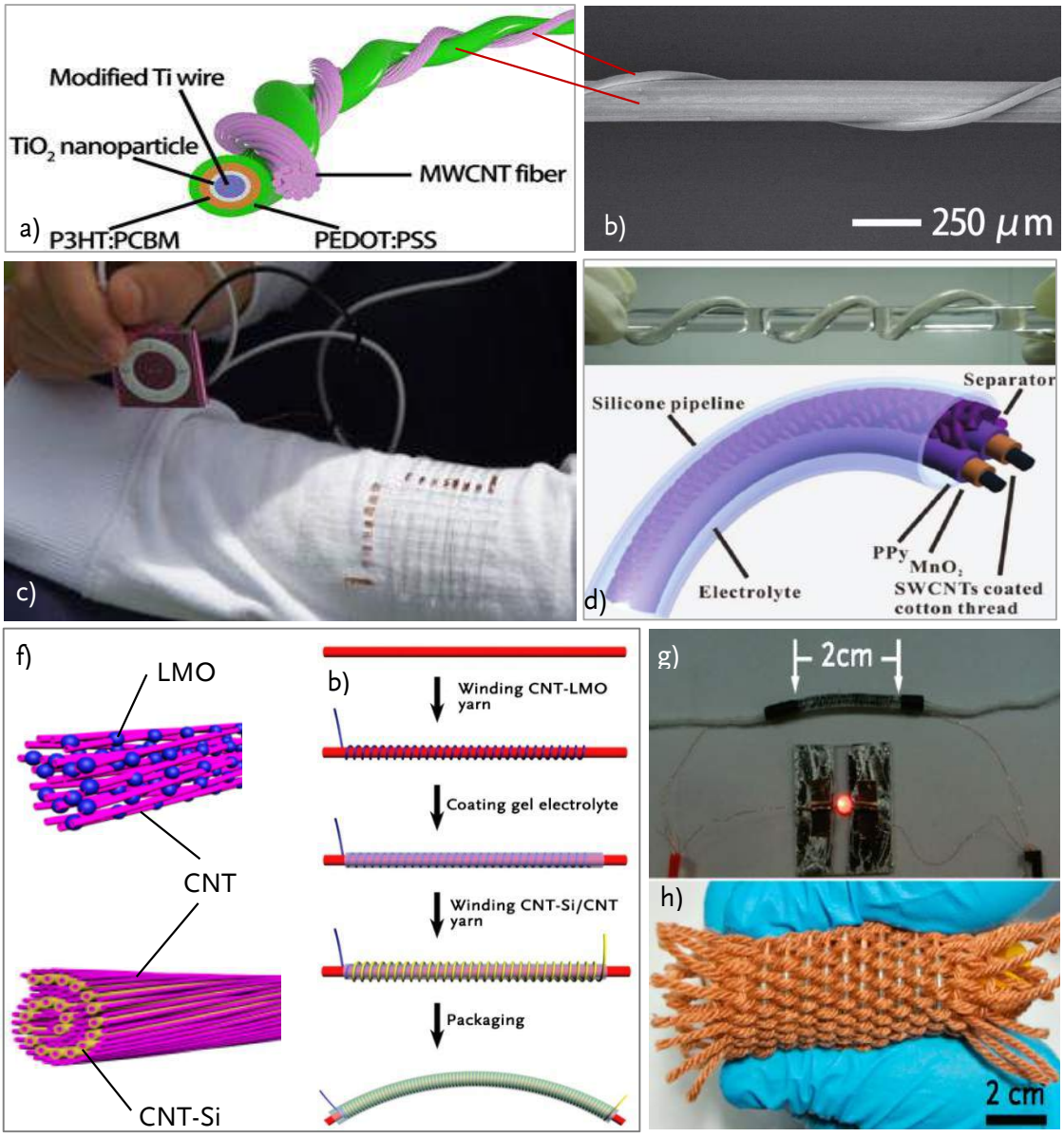


Fig. 59 – a) Illustration of polymer solar cell fiber; b) Micrograph of the polymer solar cell; c) Photo of the textile with several polymer solar cell fibers on a shirt, powering an electronic device [292]; d) Photo and diagram of a fiber supercapacitor for energy storage [293]; e) 3D representation of the LMO/CNT and CNT–Si/CNT yarns; f) Manufacturing method of the energy storing fiber; g) Photograph of the fiber providing energy to lighten a LED; h) The fiber woven into a textile (grey color)[295]

Self-Cleaning coatings

Ganesh et al. [296] published in 2011 a review concerning self-cleaning coatings where the two great groups of these materials, hydrophobic and hydrophilic are analyzed. These functions come mostly from the roughness of surfaces, either making a rough surface from a low surface energy material or modifying a rough surface with a material of low surface energy (**Fig. 60**).

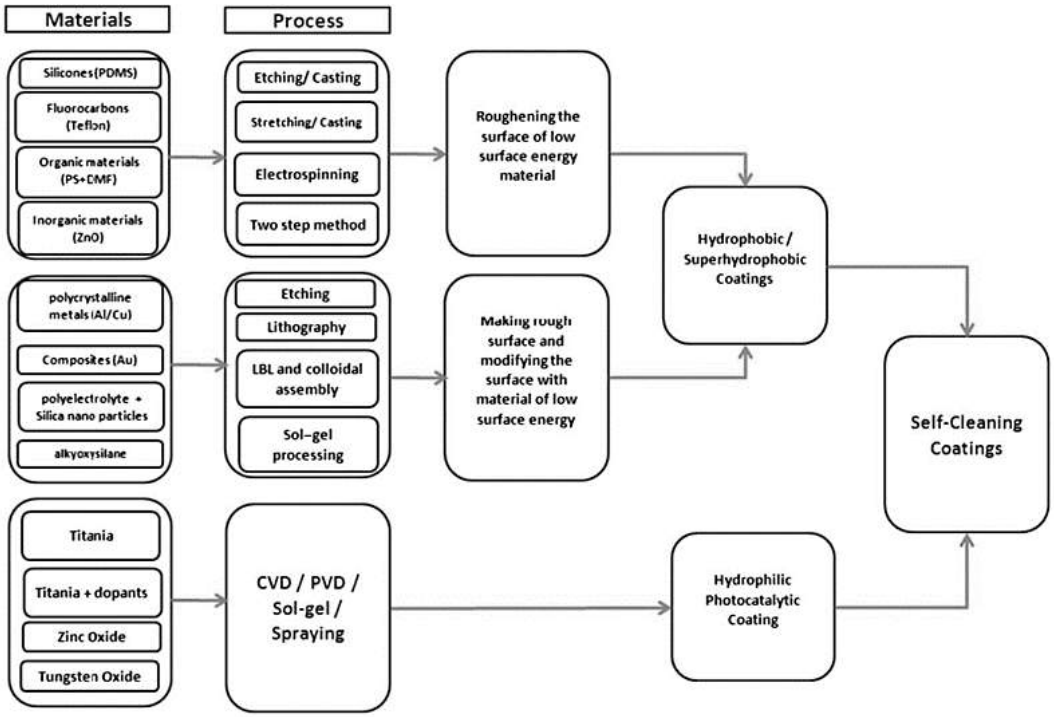


Fig. 60 – A flowchart showcasing current materials and processes used to create self-cleaning coatings [296].

Wu et al. [297] later presented a different approach by dispersing microcapsules in and onto a polymeric matrix. The ones filled with hexamethylene diisocyanate exhibited self-healing and anti-corrosion abilities. The anti-corrosion function activates when the microcapsules fracture releasing the hexamethylene diisocyanate that react with water or moisture to form polyuria that fill the crack and provide anti-corrosion (**Fig. 61**).

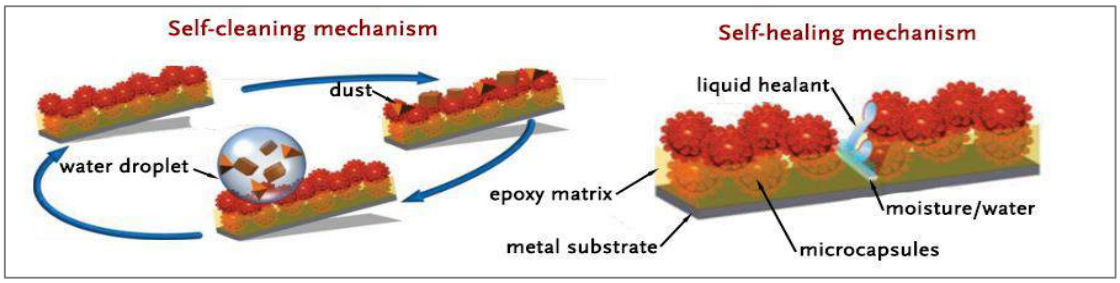


Fig. 61 – An illustration of the self-cleaning and self-healing coating produced by Wu et al. [297] (adapted).

Other examples will also be given later in the chapter Nature as a Source of Inspiration, since many self-cleaning mechanisms are biomimetic in their nature.

Self-Healing materials

Self-healing materials are materials that are capable of self-repairing damage without human intervention. Not having artificial self-healing MSs is something we're greatly missing out on. To give the reader a perspective, the fatigue life of human tibia would be less than three years if the self-healing mechanism was not present [298]. There have

been written reviews [299-302] and even books about this topic [303-305], so here only but an overview is presented.

Whereas in living beings these processes seem self-evident – merging of broken bones, healing of blood vessels and skin – in machines, structures and devices, the materials generally do not possess this ability. Things are mostly designed on the basis of the damage prevention philosophy instead of damage prevention and management. Currently, and contrary to living beings, we can only restore the function of a fractured parte, and not the microstructure in a way that it would be undistinguishable from what it was before damaged.

To help categorize these materials we can divide them into classes (**Fig. 62**). The first is related to how the healing mechanism is triggered. If it needs an external stimulus such as light or heat they're called non-autonomic, whereas if the damage itself is enough to trigger the healing they're called autonomic. The second is related to how the healing mechanism is or isn't part of the material. In extrinsic self-healing, the process requires external, specifically brought in by vascules, or embedded in micro or nanocapsules materials for the self-healing to occur. Intrinsic self-healing, on the other hand happens when the matrix itself has the ability to provide healing function.

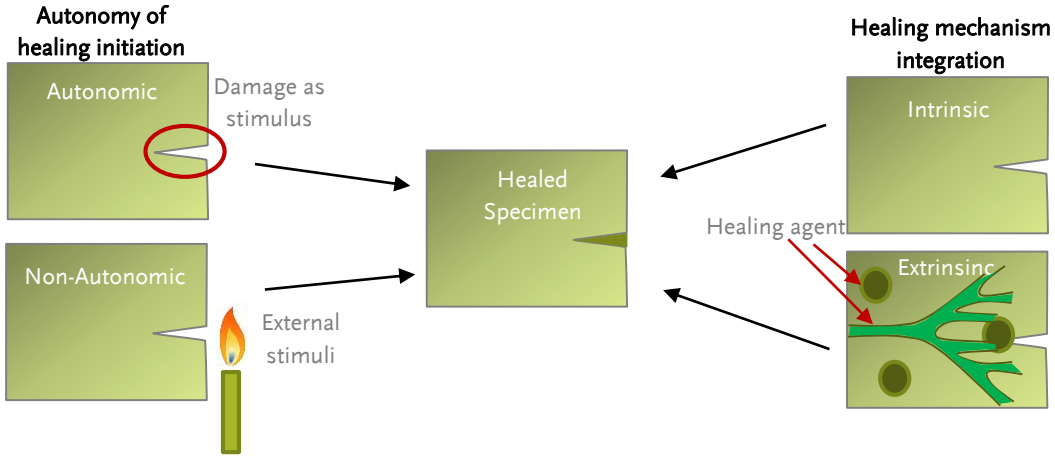


Fig. 62 – Classification of self-healing materials according to their autonomy and healing mechanism integration.

The self-healing ability has been studied in for ceramics, metals and polymers. A way to quickly perceive the difference in difficulty of implementing the self-healing functions on these three material types is through the temperatures at which the mechanism of healing occurs. Low temperatures for polymers and their composites (< 120 °C) and high temperatures for metals (< 600 °C) and ceramics (> 800 °C). In **Table 5** a brief summary is presented of research concerning each material, the healing methods studied, and the type of healing method according to the classification presented before.

Table 5 – Summary of the research papers concerning ceramics, metals and polymers and their composites.

Healing method	Autonomy of healing initiation		Healing mechanism integration	
	Autonomic	Non-autonomic (stimulus)	Intrinsic	Extrinsic
Ceramics and their composites				
SiC Oxidation [306, 307]	✓		✓	
Metals and their composites				
SMA + off-eutectic [308]		✓(thermal)	✓	✓ (SMA wires for closing the gap)
Low fusion temperature alloy [301, 308, 309]		✓(thermal)		✓ (hollow tubes, microcapsules)
Precipitation [301]		✓ (thermal)	✓	
Inductive and Resistive heating for SMA activation		✓ (electrical)		
Electrochemical [301]		✓ (electrical)		✓
Polymers and their composites				
Supramolecular-based Polymers [310, 311]		✓ (mechanical)	✓	
Diels Alder polymers [312, 313]		✓ (thermal)	✓	
Electrical resistive heating [314]		✓ (electrical)	✓	
Organometallic polymers [315]		✓ (electrical)	✓	
Sensitive to heating through electro-magnetic induction		✓ (electro-mag-netic)		
Ionomers [316]		✓ (ballistic)	✓	
Sensitive to opto-chemical reactions [317]		✓ (UV radiation)		
With healing agents circulating in vasculature [318-320]	✓			✓ (vasculature)
With microcapsule filled healing agents [321]	✓			✓ (microcapsules)
With encapsulated solvents[322]	✓			✓(microcapsules)
With healing agents contained in hollow glass fibers [323]	✓			✓ (hollow tubes)

For a more detailed table exclusively for polymers please refer to [324]. Next let's discuss each with a little more detail.

Ceramics and their composites

Though it is reported to have been observed for other ceramics [325] it is about SiC that most reports focus on in terms of the self-healing ability. A recent review has been done on structural ceramics' self-healing ability by Madhan et al. [300] and Gosh's Book [303] also provides an overview. Currently the main self-healing mechanism used for ceramic-matrix composites is intrinsic and non-autonomic oxidation-induced self-healing through the increase in volume of SiC when oxidized. What happens is that the SiC on the surface of the crack, when contacts with O_2, and at high temperatures (1100-1200 °C) oxidizes and increases in volume sealing the crack (**Fig. 63**). There are still other less

researched mechanisms, but most still require temperatures higher than working temperature [299].

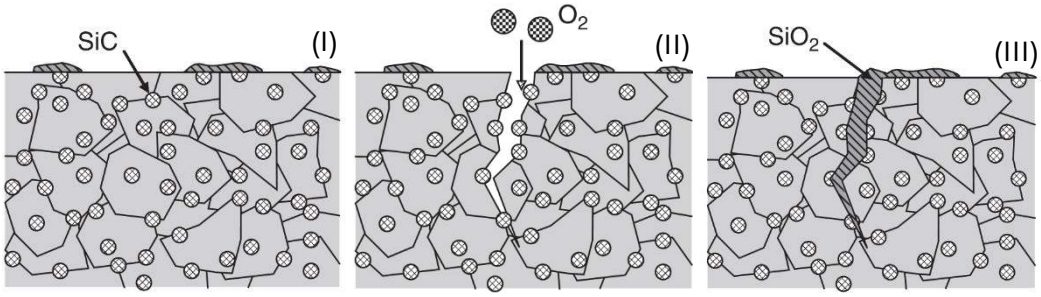


Fig. 63 – Crack healing mechanism driven by SiC oxidation [303].

In civil engineering, concrete is the most researched material for self-healing potential, and it has seen an exponential increase in interest in the last decade. In concrete, the problem that arises so much interest lies in the crack formation and possible corrosion to the reinforcing steel rods that occur as a result, which weakens the structure. Moreover repairing such damage is time consuming and costly and depending on the nature of the building may be hard due to low accessibility.

Currently there are 5 self-healing mechanisms being studied for concrete (**Fig. 64**). Herbert et al.[326] have provided a review and comparison of those methods and some considerations to have for their implementation to be successful.

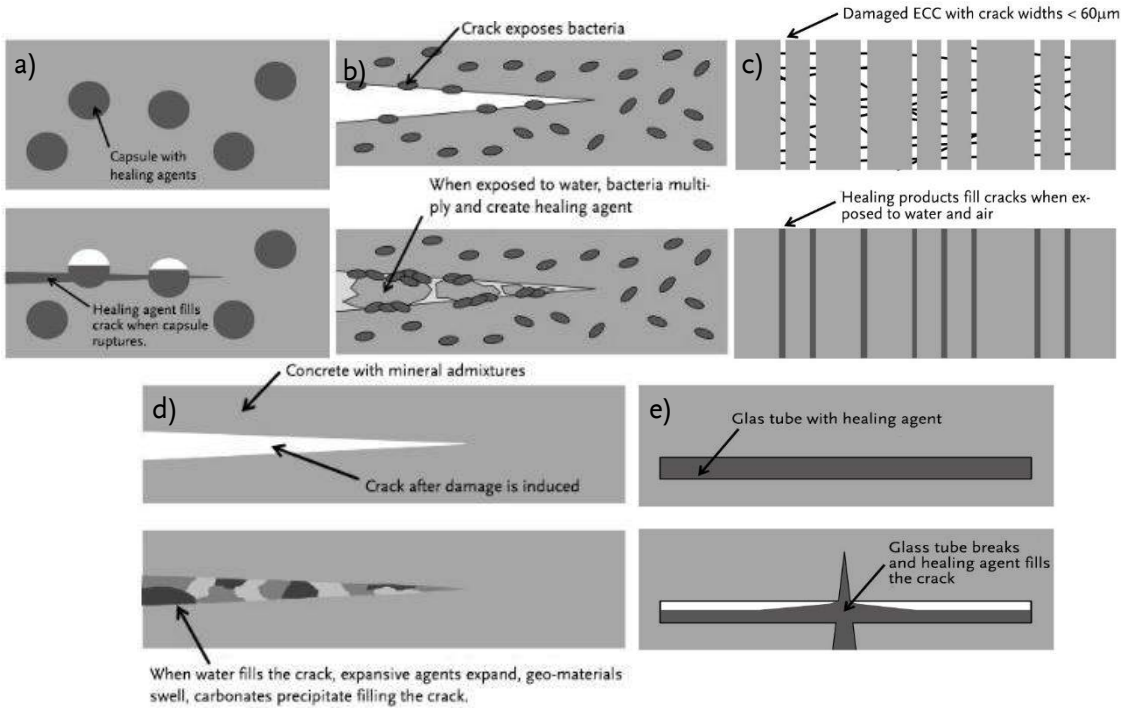


Fig. 64 – Concrete self-healing mechanisms currently being studied: a) chemical encapsulation; b) bacterial encapsulation; c) mineral admixtures; d) chemical in glass tubing; e) and intrinsic healing with self-controlled crack width. Adapted from [326].

Metals and their composites

In metals, self-healing has seen very limited success. This is because of strong atomic bonding, high fusion temperature and reactivity. The self-healing in these materials so far has been achieved and/or studied by:

1. The use of SMA wires to close cracks in combination with an off-eutectic healing system, that is, a hypoeutectic or hypereutectic composition where at the same range of temperatures that the SMA is activated, the matrix partially melts allowing the crack to be welded upon cooling [327];
2. Having a lower fusion temperature alloy melt to fill in the cracks on a higher temperature fusion alloy [301, 308, 309];
3. Manipulating the precipitation process in a metallic solution [301, 328].

Polymers and their composites

Where self-healing finds most interest is, by far, in polymer matrix composites. In them, internal micro cracks/damages during their lifetime cycle are very hard to detect and to repair. The current way to deal with this is to adopt conservative designs, which lead to overweight structures that do not utilize the full potential of fiber reinforced polymer matrixes.

The development of self-healing in thermosets has followed a distinctly different route than that of thermoplastics. While for thermoplastics healing is generally associated with the high chain mobility which allows a softening and flow of material across a damaged interface that occurs upon heating, for thermosets such is not possible because their typical cross-link network prevents the polymer chains from diffusing through the material when heated above the T_g and instead the material degrades.

Because of this, for thermosets most of the methods developed thus far are extrinsic, requiring the use of a healing agent to mend the cracks. The research is presently focused on discovering the best distribution method and healing agent as well as the possibility of mixing in others. As for the distribution method of the healing agent the most well-known are:

1) Healing agent sealed in discrete micro-capsules for one time local healing when capsules are ruptured [329](**Fig. 65 a**). This only works for micron-sized cracks with limited size and the healing process ceases once the healing agent is used. In addition, since it is a polymerization process, instant healing is difficult to achieve [18];
2) Hollow fiber embedment, generally glass fibers but more recently CNTs have also been researched [330] (**Fig. 65 b)**. This method allows for multiple healing to occur and for larger cracks, and also can increase structural performance as the fibers also have load bearing capacity;
3) A bio-inspired network of capillaries in which healing agent flows inside for multiple local healing events (**Fig. 65 c**) [318, 331, 332];

4) Brownian motion induced polymer chain crawling has also been applied for self-healing but with limited achievement [19–21].

Let's see each of the first three healing mechanisms in more detail.

One early development of the microencapsulated healing agents was developed by White et al. [333] for polymer composites. The healing agents would fill the cracks by capillary action and a catalyst dispersed within the polymer matrix would polymerize the agent when they contacted, bonding the crack interfaces.

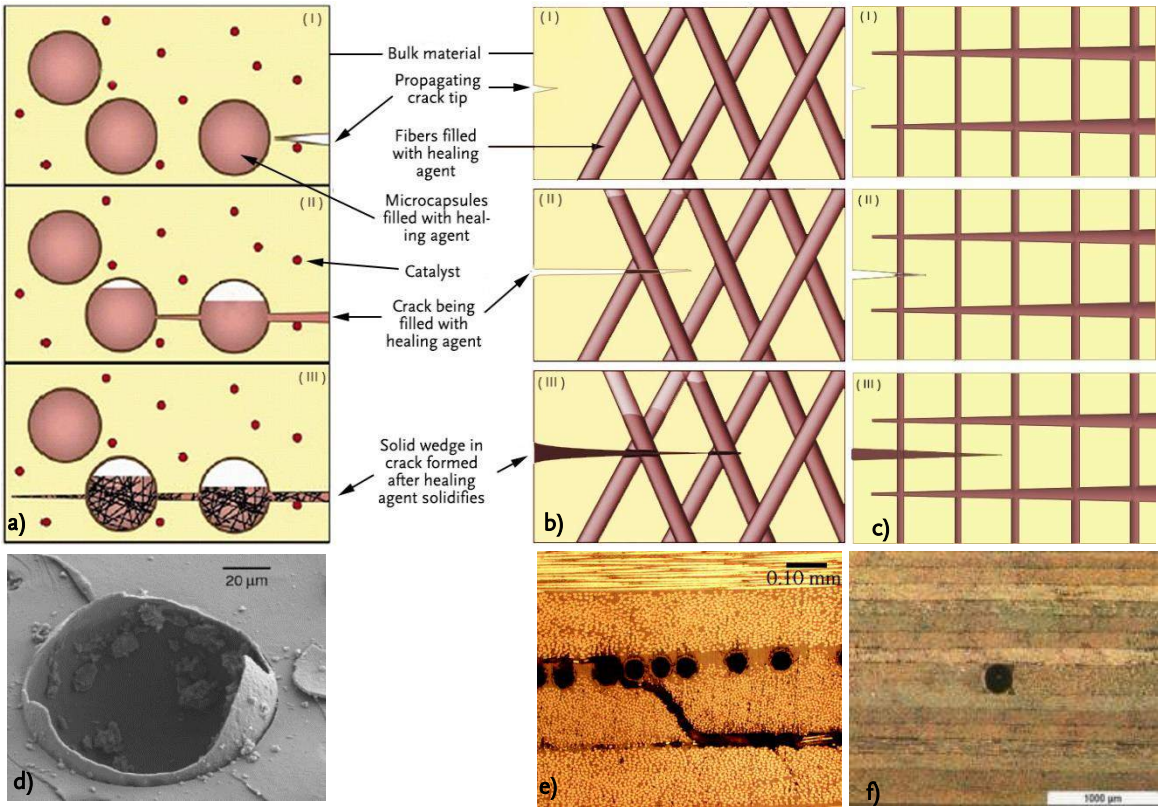


Fig. 65 – a) Illustration a self-healing mechanism based on a microencapsulated healing agent embedded in the matrix. When a crack occurs, the healing agent fills it cracks by capillary action, and, mixed with the catalyst, is polymerized and bonds the crack faces together; b) illustration of self-healing mechanism in hollow fiber-based self-healing composites. Adapted from [333]and [334]; c) Self-healing mechanism based on distribution by vasculature; d) ESEM image showing ruptured microcapsule [335] e) Intra-ply shear cracks intercepting hollow glass fibers in a self-healing CFRP laminate[336]; f) Vascule in an Epoxy/CF laminate[320].

The efficiency of the healing, in terms of fracture toughness mode I, can be defined as [333]

$$\eta = \frac{P_{healed}}{P_{virgin}} = \frac{K_{IC\ healed}}{K_{IC\ virgin}}$$

Where P is the loading and K_{IC} the fracture toughness in mode I.

With this in mind, using the tapered double cantilever beam test in **Fig. 66 a** the healed specimens were able to attain up to 75% efficiency.

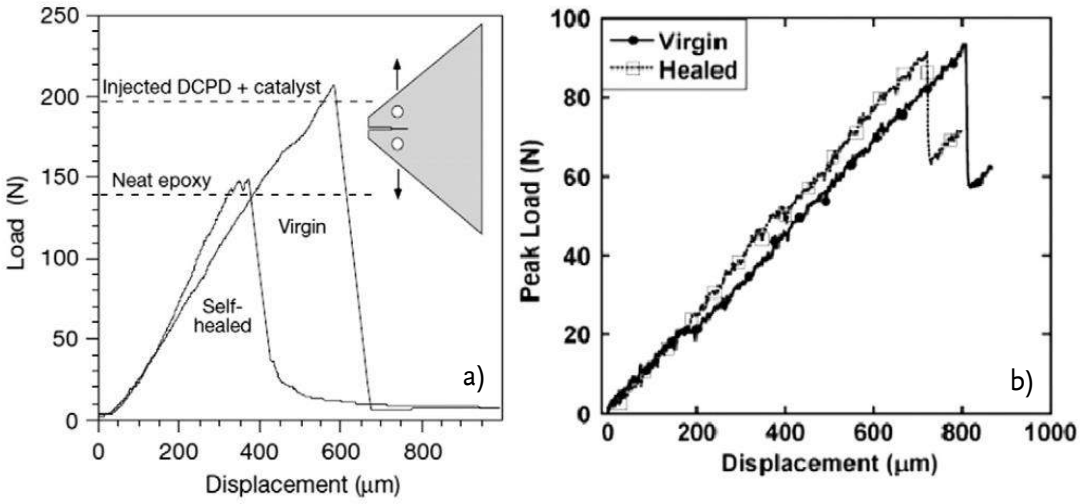


Fig. 66 – a) Load–displacement curves of virgin and self–healed specimens for mode I fracture toughness tests with microcapsules containing only epoxy–solvent healing agent[333]; b) The same but with the microcapsules containing a mixture of epoxy monomer and solvent instead [337].

Further research in epoxy-based composites has shown that including epoxy along with the healing agent in the microcapsules increases the efficiency to 100% as shown in **Fig. 66 b** [337]. Fatigue [338-340] and low-velocity impact [341] tests have also been done, as well as repeated self-healing [342].

Various healing agents have also been tried such as nanoporous silica capsules [343], nanoporous glass fibers [344], Scandium(III) Triflate [345]. Williams et al. even tried to use the self-healing polymer itself as the matrix in carbon fiber-reinforced composites by for aerospace applications [323].

Hollow fibers have shown to exhibit similar levels of performance in CFRP [323] with the added advantage of allowing for multiple healing and having less parasitic effects on the composite due to their load bearing capacity.

As for the vasculature mechanism, a simple vasculature design incorporated into a FRP via a "lost wax" process was found to facilitate a self-healing function which resulted in an outstanding recovery (≥ 96%) in post-impact compression strength. The process involved infusion of a healing resin through the vascule channels [318] and was inspired by the bone's self-healing mechanism.

The current common way of incorporating vascules or vessels, which are nothing more than tubular holes in the composite through which a healing agent can go through, is to lay low melting point solder wire between the piles of the laminates during stacking. Then it is removed post-cure in a process similar to lost wax. Norris et al. [318] has presented another other slightly different method where a portion of the ply is cut to leave a space for the vessel and tested both methods against compression impact.

One of the main challenges concerning these technologies is to minimize the parasitic effect in terms of load bearing capacity due to the vascule incorporation which also should be aligned with the local fiber orientation [318]. The next step would be to move from 2D planar vascules to 3D interconnected vascular network across multiple length scales. In natural systems, the level of vascular interconnectedness and complexity is formidable, but in engineering we're still seeing the first steps towards such accomplishment. For example Patrick et al. [319] developed and tested two architectures of 3D vascular systems with a circulating healing agent for a composite of epoxy/E-glass fibers having managed to heal delamination damage multiple times and increasing the composite's resistance to delamination initiation and propagation each time (**Fig. 67 b**). The proposed life cycle for such a self-healing polymer would be the one depicted in **Fig. 67 a**. After delamination damage occurs, vascules where two healing agents circulate are ruptured. They rush into the crack gap reacting with each other resulting in polymerization and consequent recovery of the fracture resistance.

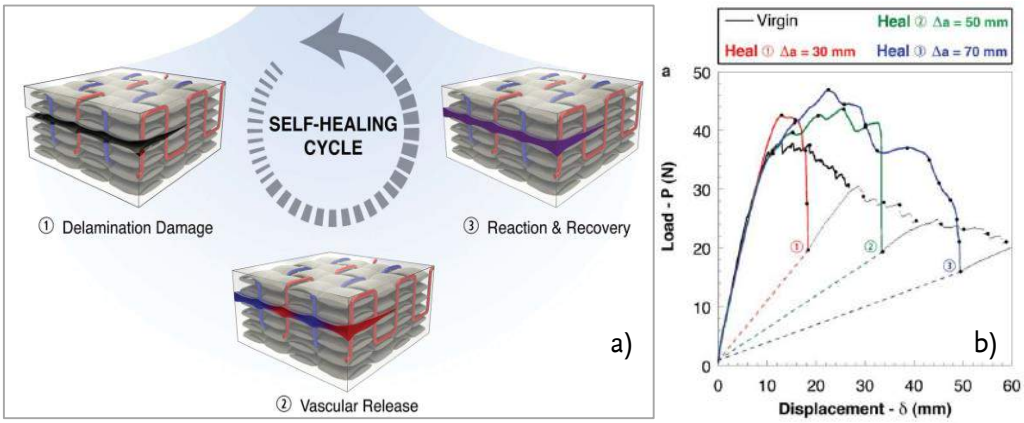


Fig. 67 – a) Proposed life-cycle of self-healing microvascular fiber-reinforced composite by Patrick et al.; b) [319].

Even if self-healing occurs and is shown to totally restore strength, it might be useful to have indications of the location and severity of the damage. Such can be accomplished if the healing agent is mixed with a fluorescent dye like Pang et al. did [346].

As the literature review showed, self-healing currently almost exclusively deals with repairing the structural function of materials. Still, when damage occurs in multifunctional composites, several functions can be impaired at the same time, which raises the need for the healing ability to repair them as well. For now this remains but a prediction of what it will be, as there don't seem to be much research going on about this yet exoteric topic.

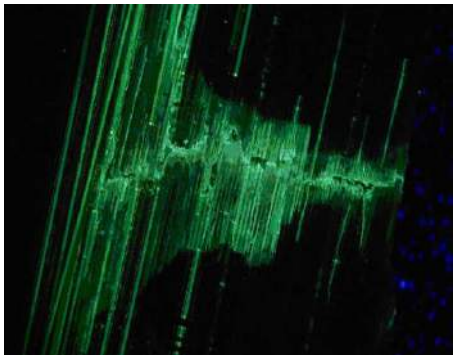


Fig. 68 – Damaged hollow fiber composite material viewed under UV light shows “bleeding” of the fluorescent dye mixed with the healing resin [346].

CHAPTER 3

Challenges in Adopting Multifunctional Material Systems

3.1 Introduction

As the state-of-the art research revealed, MFMS are still in their infancy. There are a few applications, many promising material systems but a lot more of potential.

Many challenges have been presented so far, concerning existing MFMS. For example, it was mentioned the issues concerning alignment and good dispersion of CNTs, difficulties in large scale manufacturing of graphene, issues concerning manufacturing hierarchical structures, low actuation rate of SMMs among many others. In this chapter, we're concerned about challenges of MFMS in general, and also grouping the topics mentioned throughout the previous topic into general groups. So we'll talk about manufacturing, developing new MFMS and their needs, the increasingly higher multidisciplinary requirements, and environmental and sustainability issues.

3.2 Manufacturing

Key enabling technologies (KETs) are technologies which drive innovation in the present and that have potential to do so in the future. They contribute to the development of disruptive technologies. KETs include photonics, nanotechnology, advanced materials and biotechnology, which are all directly related with MFMS.

Currently the EU has great R&D capabilities in some KETs. However, a report by the European Commission states that the EU's major weakness is the translation of its technical knowledge into goods and services [347, 348]. For example, despite the EU being a dominant force in patent fillings, those are increasingly being more exploited outside the EU. This gap between knowledge generation and its commercialization is known as the 'Valley of Death'. The technology transfer process between research institutions should be strengthened, but there seems to be an issue that is slowing this down which is the loss of manufacturing share to other countries mainly in Asia.

A similar issue can be seen in the USA where recently (May 2011) President Obama's advisory panel on science and technology was tasked with the elaboration of a strategy aimed at reviving the country's manufacturing sector. One of the concerns expressed was that the U.S.'s innovation system was being compromised by the loss of manufacturing to other countries. "As manufacturing goes, so too will design and R&D," they said.

In Europe KETs-related manufacturing is decreasing [349]. This creates some problems. In the short term, related to job creation and opportunities for growth, and in the long term, knowledge creation since R&D and manufacturing are mutually reinforcing often taking place in close proximity to each other.

I don't believe we should do this as a competition with the other nations, in the sense of being better than the others, but as a way to improve EU itself and by drag, the world.

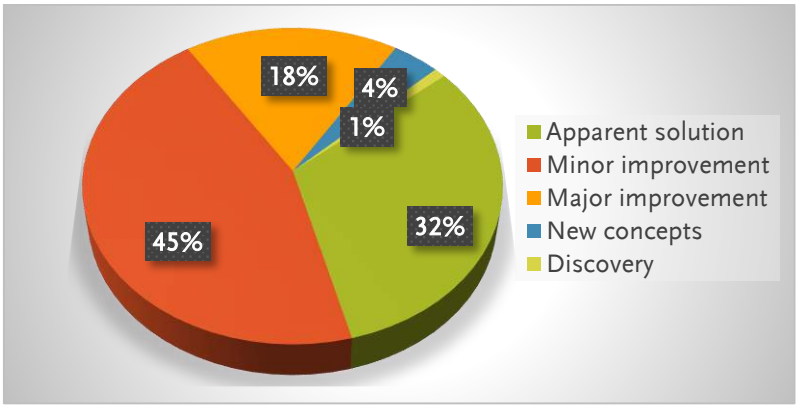
Innovation in manufacturing is a whole topic by itself, and one that as we just saw is important to set minds focused on. And so is the next topic, which is concerned with innovations before the manufacturing phase.

3.3 Innovative Material Systems Development and Integration in Products

Idea generation

A great part of the challenges in the development of products that have MFMS are concerned with the material systems themselves. And the first step is the idea generation process, or ideation.

When creating a new systematic approach for engineering problem solving, Genrich Altshuller reviewed over 40 thousand – now up to 3 million thanks to his followers – patents in the 70's and he was able to discover the proportion of developments arising from different types of knowledge (**Fig. 69**) [350].



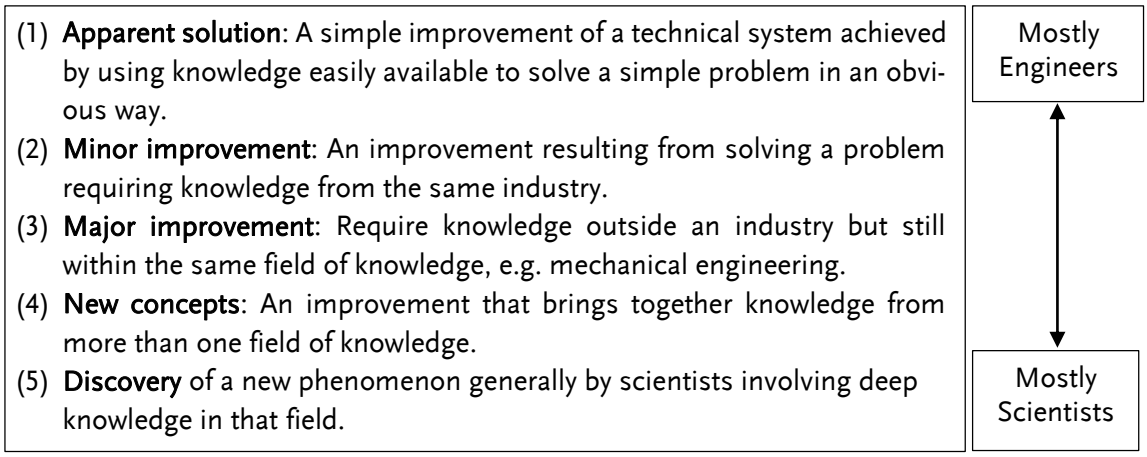


Fig. 69 – Levels of innovation on which new engineering patents are based on. Data from [351].

This is important because there are plenty of life-changing innovations out there waiting to happen, that **don't** require new scientific discoveries but simply connecting bits of knowledge already available. Take for instance 15 year-old Jack Andrakas that won the Intel International Science and Engineering Fair for $70k that used a combination of knowledge of CNTs and antibodies to come up with the idea of an inexpensive pancreatic cancer blood test.

Or the bagless vacuum cleaner invented by James Dyson that used cyclone separation. This technique was a novelty for vacuum cleaners but it was a well-established one for other industries such as saw mills since the 19th century [350].

Or Jake Dyson's adaptation of a cooling system used in satellites to cool down LEDs, where heat has been the main impediment to increase their lifespan for many years [352].

As for material innovations, we have very advanced technology that is used every day by all living organisms which certainly has solved many problems that we are still trying to, in terms of material and energetic efficiency as well as multifunctionality.

So in the ideation process the lack of available knowledge is not a problem per se. Rather, the problem is in finding and organizing the knowledge that is available and appropriate to solve specific problems or inspire new solutions.

Needs of MFMS and their Performance

A new material, alloy or composite should satisfy certain requirements for being deemed useful and sustainable and environmental healthy for the applications it is to be used on. The following are some of those requirements:

- Engineering
  - Mechanical, electrical, thermal, chemical characteristics such as strength, ductility, fatigue strength, chemical stability, electric and thermal conductivity, … ;

- Related to manufacturing:
  - Necessary equipment for production – does it require expensive, and very specific machines?
  - Is it scalable for production in large scales?

- Economic
  - Raw material costs and logistics – is it toxic, explosive or highly flammable? if so, it will need careful transportation;
  - Machine maintenance and running costs;
  - Energy requirements;
  - Production costs – can it be automated and produced in large scales?;
- Sustainable development criteria and environmental characteristics:
  - Reuse and recycling capacities;
  - Availability of raw materials – consider asteroids as well;
  - Toxicity of raw and final materials and of waste products;
  - Embodied energy and CO_2 footprint;

If a material system meets these requirements to be fully accepted into an industry ideally it would also need to satisfy the ones on **Table 6**.

Table 6 – Requirements to increase a new MFMS adoption rate in the industry. Inspired from [353].

I – Information	(I_1)	Extensive and reliable property data provided by the manufacturer
	(I_2)	Literature offering detailed descriptions of product development using MFMS.
	(I_3)	Networks involving scientists and engineers including from areas such as biology, environment and medical.
P – Performance	(P_1)	Equations that describe the MFMS behavior.
	(P_2)	Equations that describe system-level efficiency depending on the included functions'.
M – Material and Structural	(C_1)	Stable properties. It can be consistently manufactured in order to obtain the desired properties.
D – Design Tools	(D_1)	Design guidelines, such as guidelines regarding fatigue protection, control of operating temperature, joule heating.
	(D_2)	Design tools describing the functional behavior, such as computerized constitutive material models, product geometry models and material property databases.
O – Operation	(O_1)	Adaptive systems measuring the changes of material or product behavior and adapting the operational conditions to the properties and / or behavior changed.
S – Standardization	(S_1)	Standardized nomenclature (material 1/material 2-function A, function B, hierarchy if applicable...)
	(S_2)	Standardized test procedures for each function.

I believe P_2 to require some further explanation. Knowing how system-level efficiency varies with the added functions is very important because it is the first step in the decision whether to include multifunctionality in the design. Even more so in high performance systems where a total system's performance change by the inclusion of MFMS

isn't clear. Sometimes this may need performance estimates for both the design with unifunctional and multifunctional components which can be a challenge without going through two separate design and build stages. This is made more complex when systems have more than one objective. For example, UAVs have a simple quantifiable system metric that is flight endurance time and a wide range of software and databases that can be used to predict accurately that metric based on given parameters. But, for example, a family automobile has multiple objectives besides energy autonomy such as comfort, power and safety which increases the difficulty reaching a conclusion of decided whether to opt to use a MFMS.

The distinct nature of the functions, and the need to assess their efficacy as well as the broad-knowledge requirement for a better ideation process also rises another issue.

Multidisciplinarity

As the number of simultaneous functions material systems are able to perform, so does the number of fields involved in their developing and manufacturing, since many functions belong to different fields of study. For example, a bio-inspired self-cleaning with energy storage and harvesting and actuation abilities might involve biologists, material scientists, electrical and mechanical engineers.

Some authors have reported that for example SMAs had no shortage of ideas for applications but it wasn't marketable for several reasons [351, 353, 354]:

1) A lot of the available information was too difficult to digest by design engineers, since it was focused on materials science;
2) There lacked material models, and design equations to guide in the design process and for the material simulation;
3) There lacked integration in finite element simulations and CAD software which resulted in the need for extensive testing prior to production;

Closer collaboration between materials scientists and engineers was needed, and perhaps other methods of information sharing and organization/treatment.

As we will see later, to increase creativity it helps to have broad knowledge about different fields. One specific case where that is important is in bio-inspired design. For example to improve this bio-inspiration, it would help to have some curriculum modules in engineering courses on bio-inspired design or even biology, structured to align itself with the rest of the curriculum of the course, as it was done in the University of Maryland for mechanical engineering undergraduate students [355]. But implementing this is a challenge in itself as professors might not see the benefits immediately.

Recyclability, Biodegradability, Sustainability and the Environment

Composites haven't yet been properly recycled due to their heterogeneous nature. The methods developed so far have high energy requirements and/or end up with low quality recyclates. Nowadays, the products at the end of their life see the composites they're made of down recycled, that is, used as fuel for energy recovery systems [356]. Still, it is unclear how similar to current composites, especially to the most used ones CFRP and GFRP, will be the multifunctional composites of the future. If current MFMS are of any indication, then they will be harder to recycle, because of the even greater number of distinct materials and their higher connectedness.

A way to overcome this would be to have recyclability in mind when designing the material system. Another way to overcome this is the ability for materials to be upgradable, so that new technologies can be implemented in existing materials. Still, these are great enough challenges by themselves. Even more so self-recyclable materials, which at the push of a button, would consume themselves originating clean energy or simply turn into a bio-degradable compound.

As a knowledge rich but resource-scarce continent, Europe needs its products to have high knowledge content and low material and energy requirements. In this regard, material systems development takes a special position because on it depends the design of new products for recycling and the recycling technologies (**Fig. 70**).

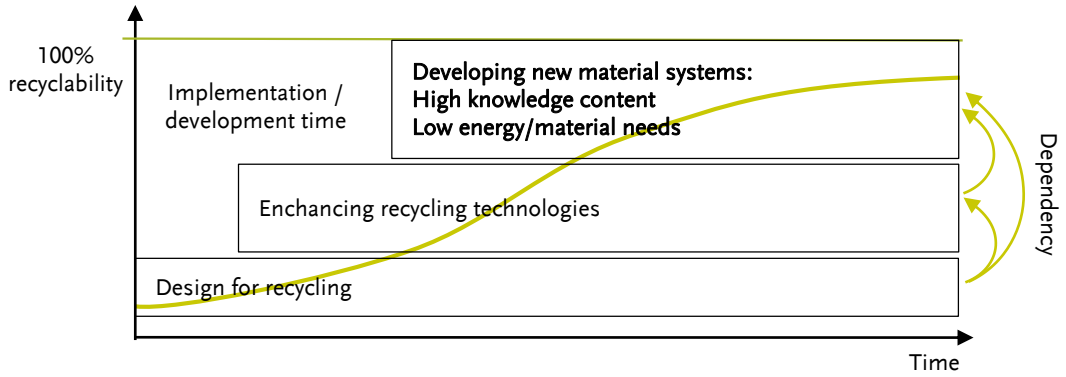


Fig. 70 – Recycling and the importance of innovative material systems. The arrows on the right represent dependency: design for recycling depends on current recycling technologies and materials, recycling technologies depend on materials.

Currently designing for recycling presents a big problem for MFMS because functions have been many times attained through the addition of distinct materials into the composite which is in conflict with the desire to separate the materials so that they can be recycled. In terms of recyclability multifunctional materials, such as CNTs and graphene, should be superior to MFCs because of this –they are a single material with several functions, so no material separation is needed for recycling. On the other hand MFC rely on

their multifunctionality to be supplied by more than one material. Other factors excluded, the lesser the number of materials there are in a MFMS the easier it would be to separate them for recycling purposes.

But recyclability isn't the whole issue. We should also think about the production of said materials, namely their embodied energy and embodied energy per time in use (embodied energy divided by life cycle) [357]. Titanium may have a high value of embodied energy (**Fig. 71**), but because of its good durability properties, if well designed, the part could last for many years and have lower embodied energy per time in use than other materials that initially show lower embodied energy values. This is important to think about because material development also needs to concern itself with durability properties in order to decrease embodied energy per time in use and therefore increase sustainability.

Also, even though a material may be more costly and have a higher embodied energy per time in use to produce, if e.g. it makes the vehicle or aircraft it constitutes lighter, it will result in a lower energy requirement for moving. If the material system incorporates other functionalities such as damage sensitivity reducing the need for external machinery for damage sensing, it provides the company with less costs and the environment a lift from the burden of having to produce, and recycle or harbor the wastes from said machinery.

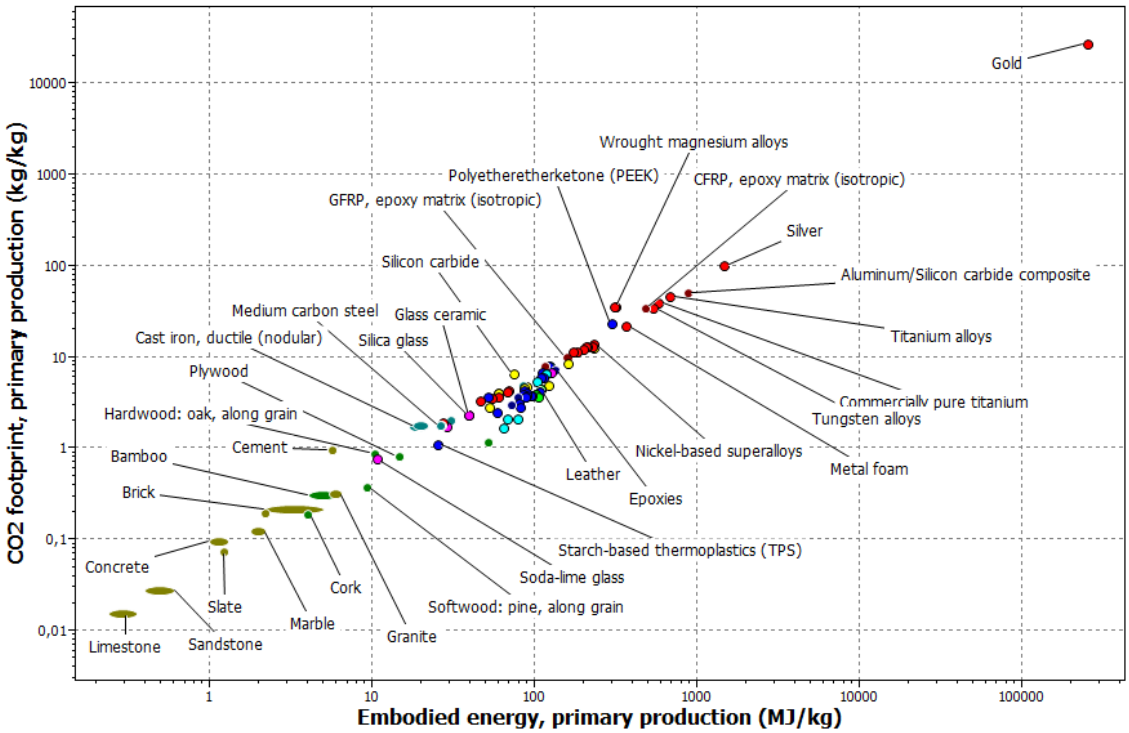


Fig. 71 – An overview of some of current materials embodied energy and CO_2 footprint [97].

The production of materials has also been highly correlated with CO_2 production, unfortunately because the energy necessary to their production often comes from burning of fossil fuels.

Therefore with the change to renewable sources of energy it is expected that CO_2 footprint and embodied energy don't correlate so well. This is a challenge indirectly related to the topic of challenges related to MFMS, because it concerns more the energy field rather that the material and manufacturing part. However, the energy field too, can benefit from the development of energy harvesting material systems, which typically use renewable sources of energy, of which the most useful for this case should be the Sun.

But even if materials are produced in the most efficient manner from renewable energy sources and their multifunctionality reduces redundancy in products and the systems' energy requirement throughout its life cycle, a lot can be wasted *during* manufacturing. There's a concept in aerospace named buy-to-fly ratio which is the amount of raw material that is bought that ends up flying. Typically in aerospace it is around 10:1[358, 359]. So they waste 90% of the material they buy, which is incredibly inefficient. Additive manufacturing would immensely improve this (**Fig. 72**), and would allow several nanoscale structures and hierarchical material systems to be produced, thus increasing manufacturing *and* material efficiency.

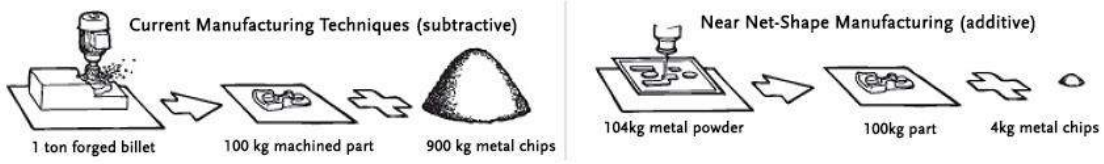


Fig. 72 – Increases can be seen in manufacturing efficiency by using additive rather that subtractive processes, adapted from [360].

We've mentioned costs, efficiency and recyclability. We're left with hazardousness and biodegradability.

Non-hazardous is the property of materials whose production doesn't release waste that is dangerous or potentially harmful to the environment or to health. A clear example is PZT, which contains lead. If present in the component contains more than 1000ppm it is considered as hazardous by the Restriction of Hazardous Substances Directive. Some of it is released to the atmosphere as PbO during PZT's production, which is one of the reasons why researchers want to replace the material.

As for biodegradability, it is especially important for products whose materials can't be recycled or are used as disposable items, and therefore the end result will be some kind of waste. It is possible to imagine that as the human race expands to living outside our planet, there will be (near?) unlimited space to leave waste, but still, are we to be

known as a space-polluting species? Nevertheless, while we're on Earth, biodegradability definitely increases sustainability, even more so for Europe as our limited space also means limited landfill space, which should ideally be close to null. The importance of this is recognized by the European Commission (EC) who have the Landfill Directive (1999/31/EC) whose purpose is to prevent and reduce the impact of landfills, with one of the main objectives to reduce the landfill space of 2016 to 35% of that of 1995 [361]. A more recent (2014) communication from the EC proposed the total elimination of landfills of EU's member states by 2030 [362]. In the same report, they propose suggestions for designing and innovating in what they call a circular economy, in which little is wasted, and a lot recirculates throughout the process from when a material first is extracted to when it is recycled and included in a new product. It also promotes designing products so that waste is eliminated, meaning that innovations related to increasing product sustainability are spread throughout the value chain, instead of relying only on solutions at the end of the life of a product.

These 5 properties – efficiency, recyclability, biodegradability, non-hazardousness and commercial viability – conclude the requirements that an ideally-approaching sustainable and environmentally friendly material would have (**Fig. 73**).

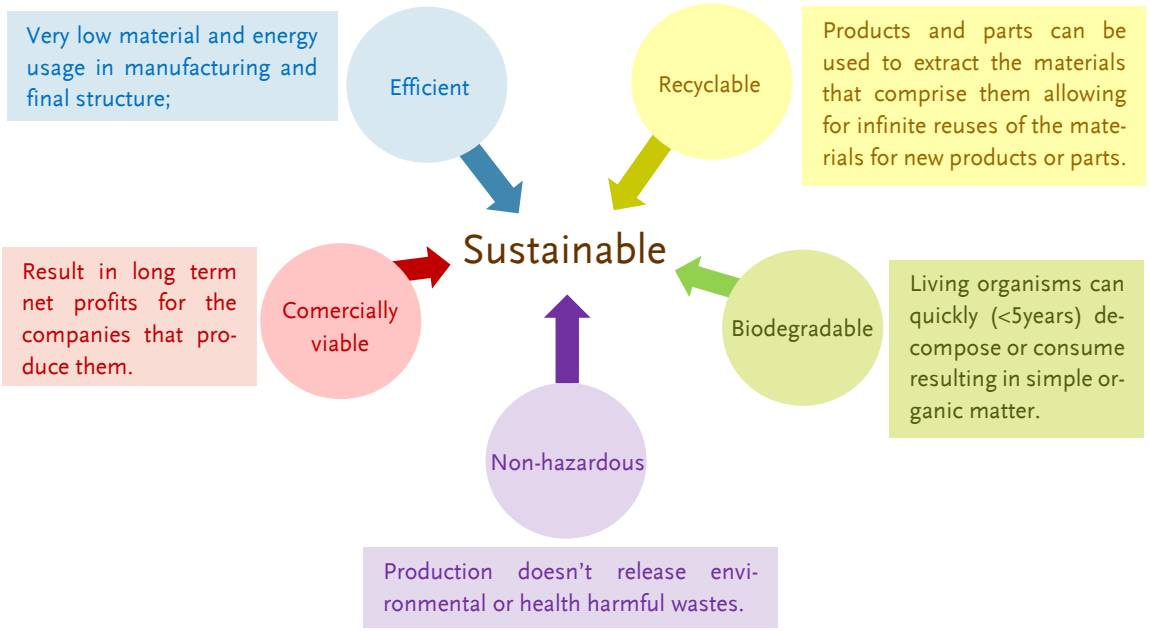


Fig. 73 – Requirements of the ideal-approaching sustainable material systems.

In **Fig. 70** we can see how recyclability depends at a fundamental level on the development of recyclable MFMS. This is the reason I believe that a key part in the adoption of MFMS with all the good properties mentioned so far in this subchapter critically depend on developing new MFMS that possess them and also on the way products are

designed. One of the ways to improve this is to develop better unifunctional MS. Another is improving manufacturing processes which currently is a serious problem in many of these materials.

On the other hand, manufacturing is material-dependent and is a huge topic in itself, and needs to be addressed as such for it to be properly discussed. Also, 3D printing is taking this industry by storm and it is possible it will change the paradigm in regards to manufacturing as well. Previously said impossible, it is now for instance possible to print complete metal parts, e.g. a full scale rocket engine part 3D printed by NASA engineers [363], 3D printed metal bridge in Amsterdam [364], 3D-printed platinum thruster chamber by ESA [365] and so on [366-368]. Or even the 3-D Printed Habitat Challenge for $2.2M in prize "designed to advance the additive construction technology needed to create sustainable housing solutions for Earth and beyond" by NASA.

In here I then decided to focus on material systems innovation and design in conjunction with innovative product development, which is already a huge topic in itself, as we're about to see.

CHAPTER 4

Sensible Adoption and Innovation of Multifunctional Material Systems and their Products

4.1 On the Idea Generation Process

General Tools that Foster Creativity

Every human that has ever lived, has lived in a different world from that of everyone else: the unique world their brain created. As each person grows, and their unique brain structure changes and experiences are lived, we create a set of beliefs and thinking patterns that the brain finds best fit to explain and to deal with all that it has observed. This results in different versions of the same objective world, for different people.

To create new useful multifunctional materials, or combinations of them, or to find ways to use existing multifunctional materials and composites in products, or to develop new manufacturing techniques, or to better take inspiration from nature, it is important to understand and improve the skill of idea generation or ideation.

This skill is often linked with the well-known expression used in innovation circles of "thinking outside the box". This implies that we tend to live inside a 'box' which is precisely the world construct mentioned in the first paragraph. Thinking outside of that isn't easy, and that's one of the reasons many companies hold idea generation contests for young people, which live in considerably different worlds that those of the typical employee of the company.

The following list was based on Davidson et al. [369] list of cognitive processes that problem solvers use when generating solutions.

1. **Divergent thinking** – thought process that consists of widening the field of ideas, to create more choices. It is the route to innovation.
    a. Creative thinking – consists on an extreme way of divergent thinking that stimulates unorthodox solutions and the adoption of radically new perspectives, this is where "outside-the-box" thinking belongs.

2. **Convergent thinking** – thought process that consists in splaying the domain of ideas to a few or one single selected option. The larger the initial domain of ideas the better the chances the selected idea will be more satisfactory.
    a. Critical and logical (deductive) thinking – consist on the main thinking patterns that are responsible for the reduction of the number of ideas.

These processes can be arranged in a time-frame (**Fig. 74**) which can be explained as follows: We start off by expanding the domain of ideas. Existing ideas may lead to new ideas (purple). These are generally created by the person's perspective, in their field of work and according to their patterns of thought. If intent is put towards creative thinking by using some tools to be introduced shortly, then radically new, "out-of-the-box" ideas can be thought of (red). Radically new and unorthodox ideas tend to widen the scope or the field of view of the ideas. For instance, if initially ideas to develop a new material system with actuation ability might only belong to PZT, they might diverge to all piezo-electrics. Someone might then suggest that we ought to take inspiration from nature, and give an idea from an actuation mechanism of a living being. This widens the field of possible ideas to biology now. And so on. After we've expanded this domain to a level that we feel comfortable that it encompasses a sufficient and varied amount of ideas, we can proceed to convergent thinking where progressive filtering occurs until a few or a single idea or solution is selected. This phase can prolong itself up until prototyping where generally the flaws of lesser solutions become more apparent.

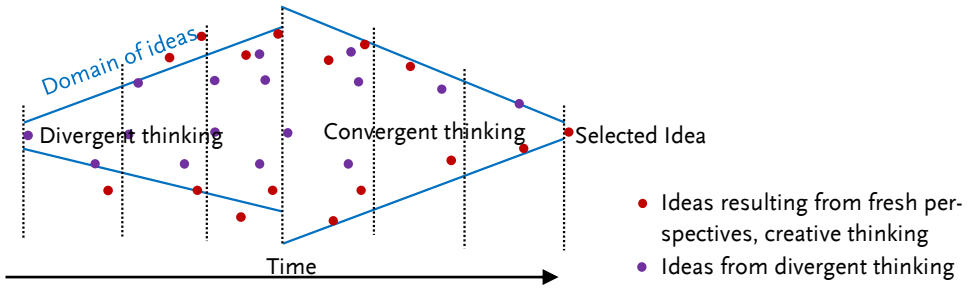


Fig. 74 – A typical thinking process of generating a solution.

Below is a list of useful techniques by alphabetical order to stimulate divergent and creative thinking. They result from the mixture of known techniques such as lateral thinking by Edward de Bono, from Tim Brown's Change by Design [370], Ulrich's and Eppinger's Product Design and Development [371] as well as other well-known techniques.

Brainstorming

The idea is simply to think about ideas following a few rules to increase its efficacy:

1) Postpone the judgement of ideas: Such judgement includes saying certain ideas won't work, are unfeasible, or that they have problems. The reason for this is that even bad ideas can serve the purpose of sparking great ideas (**Fig. 75**). This rule also helps no. 3.

2) Encourage exaggerated and wild ideas – these often allow for new perspectives to be considered, and considerably widening the field of ideas (high divergence);
3) Focus on quantity over quality – the more ideas there are, the easier it is to combine them so that new can form.

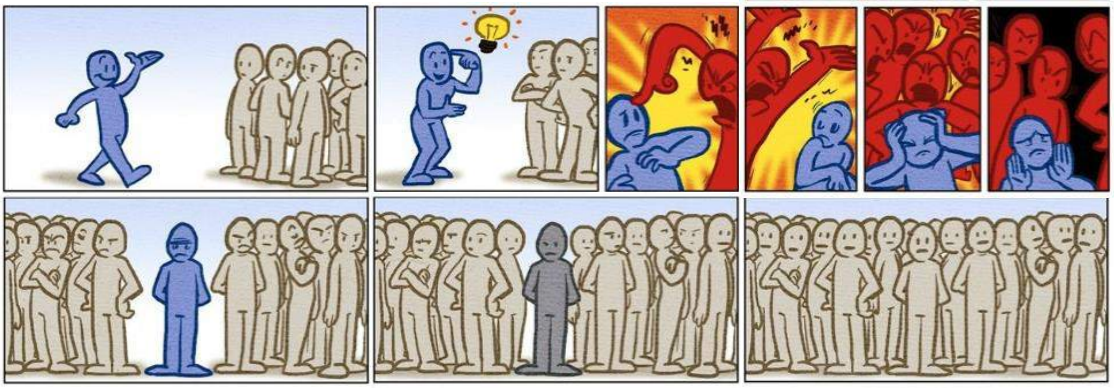


Fig. 75 – When brainstorming, welcome others' ideas, even if they sound ridiculous they can be useful in their ridiculousness in generating great ideas [372].

Brainstorming is one of the simplest idea generation tools, probably one of the most used and can often be combined with other tools to become more efficient.

Challenging the Status-quo

Asking why something exists and why is it done the way it is. See last paragraph of "First Principles Thinking".

Combining Ideas

1) Can these two things be blended? Partially, totally?
2) Can functions, principles or materials be combined?
3) How would the combination be packaged?

A quick way of generating more ideas for novel MFMS is to combine materials, structures and the method the two are connected, if applicable (**Fig. 76**). This is a solution-based approach. In **Table 7** a few simple examples resulting from this are presented.

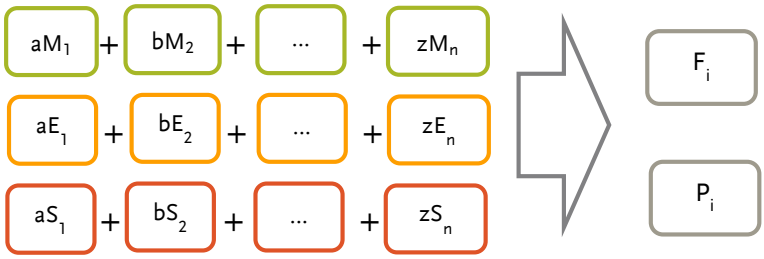


Fig. 76 – M: material; E: Method; S: structure; P: property; F: function.

Table 7 – A few examples of combinations of materials and structures resulting from creative and combinational thinking and that could perhaps yield interesting results if attempted.

Combination	Possible Desirable Function(s)	Possible Desirable Property(ies)
Aligned CNTs in a nanolattice	Structural ; Sensing	High specific strength and Young's modulus; High electrical and thermal conductivity.
Layered (PVDF + MFC + Li-ion)	Energy harvesting; Actuation; Energy storing.	Good multifunctionality
Graphene coated MFC	Structural; Actuation; Cooling;	High strength, actuation rate, thermal and electrical conductivity.
Graphene as outer layers of honeycomb structure with an elastomer and piezoelectric material	Energy harvesting; Damping	High in-plane electrical and thermal conductivity; High damping coefficient.
Fibers (CNT-Si/CNT+CNT-LMO + NiTi)	Energy storage; Actuation	High degree of autonomy
Geothite reinforced myocelium	Structural; Biodegradable	High strength and Young's modulus.
Asymmetrical PDMS tube (outside) with ZnO nanowires and polymer solar cell fiber (the one on **Fig. 59 a**) and air.	Actuation; Energy harvesting	High solar convention rate; High actuation sensibility and very low actuation force; High controllability.

Concept Fan

Start by writing the problem to solve inside a circle. To the right, possible solutions radiate. To the left, the broader theme where it belongs. From that generate other ideas (**Fig. 77**).

Connecting the Unconnected

Chose an object, a picture or any noun from an encyclopedia or on sight at random and associate it with the topic being thought about:

1) How could that help addressing the challenge?
2) How are the two related?
3) Mind map the ideas generated.

First Principles Thinking

To view knowledge as a sematic tree and making sure one understands the trunk and the big branches, i.e., the fundamental principles, before going to the details (leaves) otherwise they don't have anything to hang on to. To analyze the foundation of a problem. For example, there was a time when while many people were more concerned in improving horse carriages, rather than analyzing transportation itself. A few others, at the time, instead looked indeed at the fundamentals of transportation and saw how self-moving carriages – auto-mobiles – could in the future (our present) fulfil even better the same principles in a better way, and thus, focused on that.

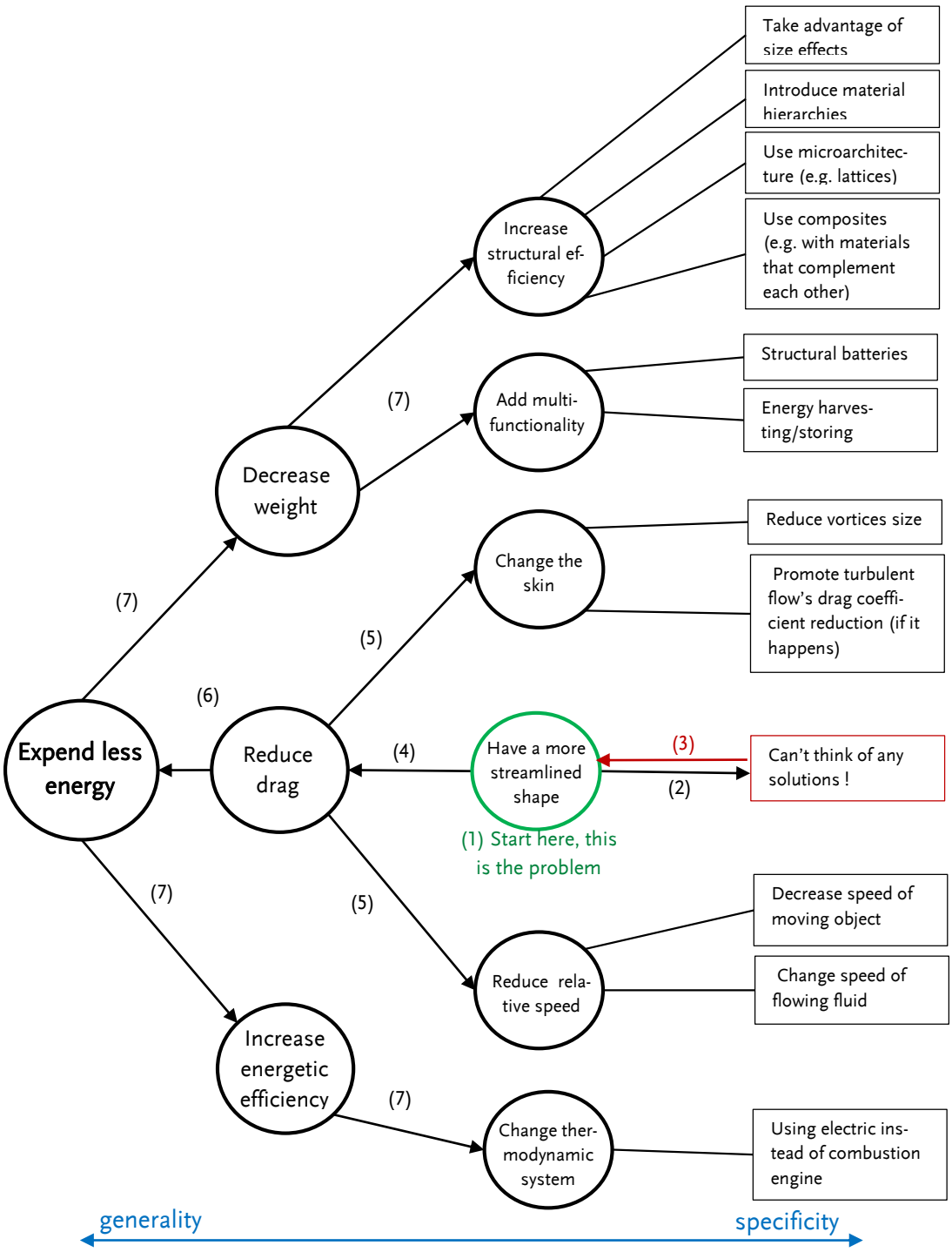


Fig. 77 – Exemplification of the concept fan for the problem of "having a more streamlined shape".

As another example, when Elon Musk and colleague engineers verified that the raw materials of typical rockets only accounted for about 2% of the total cost of the rocket which meant that the materials weren't being used smartly which lead to the going to the drawing board and completely redesign rockets. This led to the creation of SpaceX, where they were able to reduce the cost of a space rocket from 65million to about 7million, while also introducing rocket reusability [373].

This line of thinking is kind of a 'starting from scratch'. It allows one to drop all of the baggage and history that one or people that have been in the field for a long time, carry around with them, and which in the end prevents them from seeing things in a fresh perspective.

Imitating

Imitation, where someone copies the initial design but then changes it or mixes it with different designs and ends up with a better result, is often underappreciated. One of the good reasons is that those who imitate a solution might spend significantly less on R&D than those who developed it, but then can be the ones reaping most of the rewards. However, when innovators fail, it's often due to poorly executed ideas, because they always have a great head start over their competition. For example, Apple's iPad is the most famous version of the concept of a tablet, yet there had been several other earlier attempts at such product, which failed because they were poorly executed [374]. The idea was the same, the execution, and thus the final products were not. Imitation, again **not** in the sense of blindly copying, proved to be highly beneficial.

Oded Shenkar has reviewed research on breakthroughs in eight scientific fields, from neuroscience to history [375], where he observed that:

1) Imitation was a primary source of progress;
2) Good imitation requires both intelligence and imagination;
3) 98% of the value created by innovations goes to the imitators, going the other 2% to the innovators;
4) Most of the ideas weren't simply copied, they were improved upon which is what then catapulted them to success.

To a greater or lesser extend all humans are bound to imitate because that's our nature [376]. Meme's are a unit of information that multiply from brain to brain [377]. Part, if not most, of creativity comes from taking existing memes and putting them together in new ways. The greater the number of memes we have in our repertoire, the greater the chances that we can create one uniquely ours. This is a reason that supports the theory that innovation is only possible because of the gradual process of knowledge building of several underappreciated individuals, namely scientists and engineers, who despite not making Nobel-worthy discoveries, it was theirs' that allowed one in the first place.

Looking at the Extremities of the Gauss Curve

When looking for latent needs it is more important to look at extreme cases of users. For example if looking to improve kitchen utensils, it might be more valuable to observe children and professional chefs using knives. The former may reveal difficulties that adults have learned to conceal but that are still there, whereas the latter – lead users –

may reveal novel uses that could be facilitated by some minor implementations in the regular products.

Provocation

Using provocative techniques such as

1) Wishful thinking, "What if …?";
2) Exaggeration. Taking concepts to their extreme forms;
3) Reversal: Instead of thinking about how to solve a problem, or improve a composite or a manufacturing method, thinking about how to make the problem worse, the composite weaker, or the manufacturing method less efficient. Then invert those ideas. Sometimes how to make something worse is more obvious than how to make something better. But then since they are often opposites, by devising ways to worsen something, those same ways might be applied in reverse to improve them.

Separating Ideas from Concept

It consists in extracting the underlying principle behind a product or a mechanism, and looking for different ways in which the same principle could be applied. For instance, in saw mills the principle of cyclonic separation was used for several decades before someone noticed its usefulness in vacuum cleaners [350].

This tool was used in all of the study cases in the chapter "Nature as a source of inspiration".

Simple Language Reframing

Reformulate the problem with simpler language. If someone came running to you looking very distressed put their hands on your shoulders and asked: "In quick terms, how would you explain [concept/problem]?" How would you?

Shifting Perspective

Consists in asking if one were someone or something else, what would happen differently. Trying to put oneself in the shoes of the subject we're studying.

Visual Thinking

The picture superiority effect is the name of the phenomenon where memory retention and recalling is greater when the information is learned by pictures, images or graphics rather than sounds and words. This is not a 1-2% increase in recalled information, but 200-400%. This effect is well established and has been shown in various experiments in different conditions [378-380]. In fact, for the brain, letters are nothing more than pictures, and words groups of pictures with minute differences [381]. It might be a practical and easy way to provide information, but not the most effective, by far, to acquire it (**Fig. 78**).

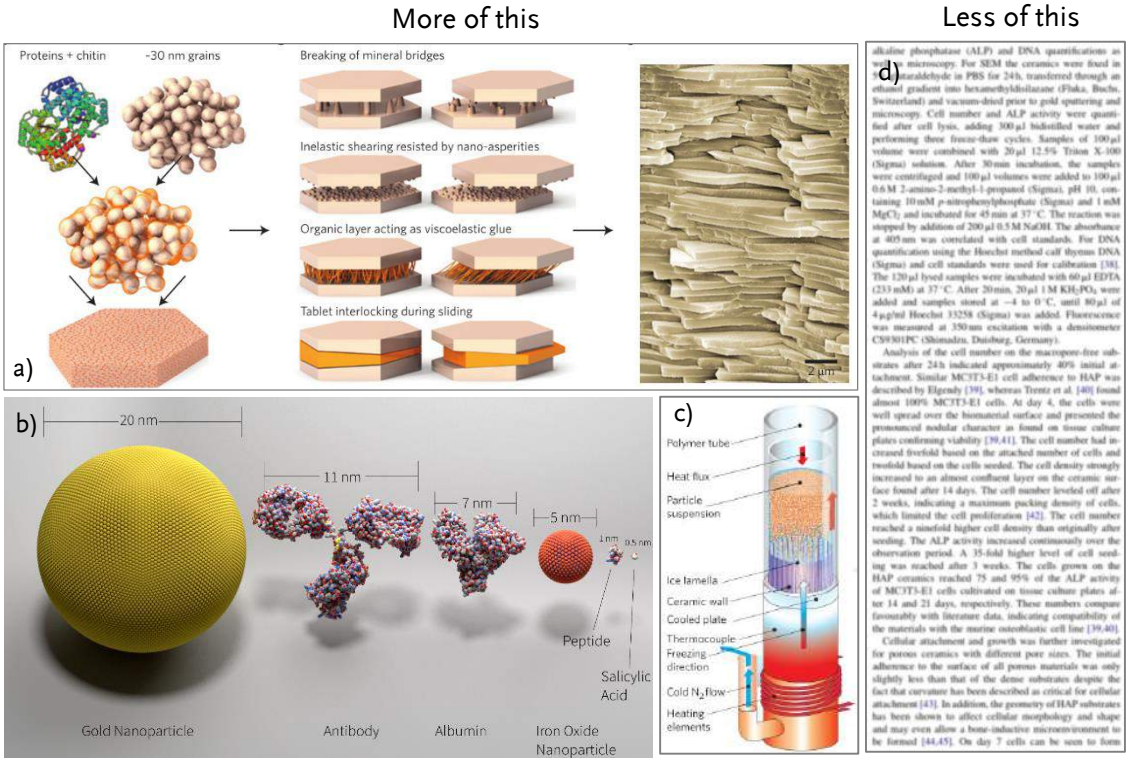


Fig. 78 – Showcasing two ways of conveying information: a–c) Examples of great explanatory images [382, 383]; d) Text.

For example in the case the subject is a person: A talented mechanical engineer, sitting down at their desk after an invigorating swim on the shore may not be prepared to design a simple bathroom appliance for their grandmother that suffers from arthritis. A thus in cases like this it is necessary to be empathetic.

Other soft-skills

- Changing environment where the brainstorming session is occurring and/or doing it while walking[2];
- Setting a culture where it's acceptable to ask forgiveness after rather than permission before, that gives permission to people to fail but still rewards them for succeeding. In such a place, there will be projects bound to go nowhere. But those are the cost to pay for the innovative projects that will. This environment is opposed to an organization where incrementalism is the norm, and therefore innovation is low but efficiency is high.
- Stay focused on the topic, have a clear motivation set in mind, build upon the ideas of others and use drawings to convey ideas;

[2] A recent study by Stanford researchers Oppezzo et al. [364] showed that walking, wherever it may it and specially in one's natural pace so as to reduce the required cognitive power to do it, significantly enhanced creative thinking compared to sitting, as tested people that walked they showed more ideas and of a more innovative character.

- Having a thick skin for failure. Human history is a list of things that couldn't be done, and then were done;
- Failing sooner to succeed earlier. Prototyping early in the product development process, so that ideas can be given a physical expression that allows designers, engineers and scientists to quickly point out faults that could be missed by only having a mental representation of the idea, and which could result in sticking with an idea for too long. It then goes without saying that early prototypes should be fast, simple and cheap, enough to allow the team to learn something and keep going.

TRIZ

Genrich Altshuller, a soviet engineer, found that existing methods of problem solving lacked structure and systematization. So in the 70's he launched TRIZ, which is the Russian acronym for 'Theory of Inventive Problem Solving' [384], a systematic approach to problem solving.

Even though TRIZ is not intuitive and its effective use requires practice and training it appears to have some success as there are companies and universities that teach this method in their engineering curriculum [350, 385].

For the purpose of product development adopting innovative MFMS I believe the following to be the most useful tools TRIZ can offer:

The software Tech-Optimizer, which is a database arranged by the functionality of several solutions. This type of software is very useful for type I-IV discoveries. For example for the function of reducing drag, there appear 30 solutions, which include using ultrasounds as is used by the chemical industry, shark skin and the saw fish in biology;

Contradiction-solving: one of the main methods used in TRIZ is based on solving contradictions, and it works like this (**Fig. 79**): let's say we are designing a product or a part, and at a certain part we reach a dilemma between two properties we want that contradict each other. For example let's take the airplane example from before. We want it to have less weight but a bigger battery, because each of them increases its flight endurance time. However that's a contradiction because a bigger battery means more weight. By going to the TRIZ Matrix and choosing the appropriate contradicting properties it would present the principle no. 40 or no. 5 (see Appendix B[3]) as a possible solution to solve that contradiction, which then should lead us then to think about having a structural battery.

[3] Even without the matrix, the 40 TRIZ principles can be very useful as a way to promote new perspectives to problem solving just by knowing of their existence, so I decided to include them here.

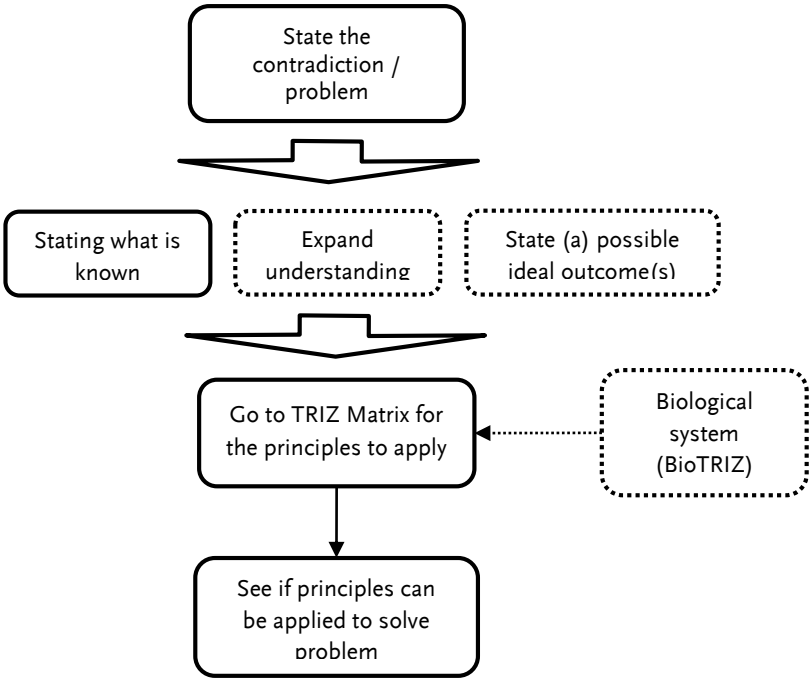


Fig. 79 – Simplified schematic of TRIZ process applied to solve a contradiction. Inside dotted-lined rectangles are optional steps.

Allowing a certain amount of time for side projects.

Andre K. 2010 Physics Nobel prize winner, said in his Nobel lecture how the graphene breakthrough was initially one of his "Friday night experiments" in which he would do side projects resulting from lateral thinking and many times read apparently irrelevant literature without any clear ideas in sight. These side projects resulted in a 10% success rate and several near misses. The successes were stunning though, including the graphene, the levitation and the gecko adhesion biomimetics. He also mentions how the properties of graphene contradict the common wisdom and how they shouldn't be possible.

Poking in new directions, even randomly can be more rewarding than common sense would led us to believe. This may be because digging too deep in well-established areas might result in diminishing returns compared to the effort that is put in. On the other hand, there is plenty of unexplored stuff at the surface just waiting for a little poke. A clear example of this is how several young fellows are able to innovate in apparently technical areas [386]. The idea of time off for side projects is probably more prevalent in tech-based companies where prominent examples such as Apple's Blue Sky [387], Google's 20% time [388] or LinkedIn's InCubator [389] give it media attention, and from which great results have come.

On Information Sharing

On paywalls and on grouping knowledge into journals

Open access is a moral imperative. Scientists and engineers do what they do for passion of technological and scientific progress, and in this age where information has the potential to reach so many, there has never been a better time to do science and engineering and achieve that objective. This potential could increase, weren't knowledge stopped from reaching eager minds. How many more discoveries and advances could be made if scientific knowledge was more freely shared among us [390]?

One of the impediments to this free share of scientific knowledge is the existence of paywalls. There are points both in favor and against their elimination and the journal method of sharing scientific knowledge, though the points in favor are immensely more numerous and, I believe, more sound [391-394].

Brembs [395] analyzed data the consequences of the current knowledge sharing system concerning various measures of scientific quality, and reached the conclusion that leaving journals in favor of another more collaborative communication system aided by the internet will be vastly superior.

In his book [396], Nielsen, a pioneer in quantum computing, argues how we're at the tipping point of a change of paradigm, a revolution in a 300-old way of doing science, driven by new cognitive tools enabled by the internet, that is resulting in a networked science, where mass-crowd-collaboration takes precedence over lone or small scientists groups.

For the readers to whom this may interest, I took the liberty to compile a few alternatives (**Table 8**). Users of these websites include scientists and engineers from prestigious universities from all over the world. I invite the reader to inform him/herself and be positively surprised.

Table 8 – Most of the descriptions were taken from the "about" section of the respective websites.

Open access archives of articles	Description
http://arxiv.org/	Open access archive, over 1million papers.
http://figshare.com/	Allows users to upload any file format to be made visually in the browser so that figures, datasets, media, papers, posters, presentations and filesets can be disseminated in a way that the current scholarly publishing model does not allow.
https://www.plos.org/	PLOS (Public Library of Science) is a nonprofit publisher and advocacy organization founded to accelerate progress in science and medicine by leading a transformation in research communication.
https://doaj.org/	It is an online directory that indexes and provides access to high quality, open access, peer-reviewed journals.
https://peerj.com/about/	Low-cost for scientists, open for all to access.
http://elifesciences.org/	The open-access non-profit eLife journal is the first step in a initiative to make science publishing more effectively benefit science and scientists.
Collaborative Science	

http://mathoverflow.net/	It is a question and answer site for professional mathematicians.
http://www.galaxyzoo.org/	It is a scientific project that has invited members of the public to help classify a million galaxies. Those involved are directly contributing to scientific research.
http://polymathprojects.org/	This group blog, together with its associated wiki, is intended to host "polymath" projects – massively collaborative mathematical research projects.
http://www.researchgate.net/	Their mission is to connect researchers and make it easy for them to share and access scientific output, knowledge, and expertise. On ResearchGate they find what they need to advance their research.
Other	
http://www.openaccessweek.org/page/about	A global event now entering its eighth year, is an opportunity for the academic and research community to continue to learn about the potential benefits of Open Access, to share what they've learned with colleagues, and to help inspire wider participation in helping to make Open Access a new norm in scholarship and research.
https://www.openaccessbutton.org/#how	Searches the web for web versions of the pdf (hosted by the authors of such papers in their own, or their faculty's website) and if it can't find, automatically sends an email to the authors asking for the file.
https://www.innocentive.com/	They crowdsource innovation solutions from the world's scientists, engineers and businessmen who compete to provide ideas and solutions to important business, social, policy, scientific, and technical challenges.

As this shift happens, authors can still license their works under creative commons attribution, meaning that authors can keep their copyrights if they wish, but readers can freely read and re-use the published work in the most meaningful manner as long as they credit the author (**Fig. 80**).



Fig. 80 – Meaning of the creative commons attributions.

For example, the 29th edition of the European Conference on Object-Oriented Programming [397] will be open access under creative commons attribution after the executive members voted almost unanimously in favor.

Awards

Awards are a great way to encourage and reward people to think about the future, and possible solutions. Knowing that we are contributing to the world becoming better is good enough motivation for many, but even then it is human to like to be acknowledged for hard work. There are several examples of this in general science and engineering areas such as the Xprize [398] and Intel International Science and Engineering Fair [386],

the Nobel prize and even material specific awards such as the James C. McGroddy Prize for New Materials [399] and the New Material Award [400], which attract lots of attention and are a great way of creating interest in innovation thinking.

More than monetary prize, they ought to serve as recognitions for outstanding achievements and devotion to science and encouragement for other people to join in on the fun.

The next subchapter is dedicated to another method of fostering creative thinking and of accelerating innovation by imitation.

4.2 Nature as a Source of Inspiration

Intro

One might argue that biological materials, with few exceptions, are worse performing than engineering materials, and are rarely used in engineering, and therefore we should dismiss nature when looking for sources of inspiration. However we have to remember that nature is very parsimonious, it has to use an inexpensive and very limited range of ingredients whose properties are often on the low-end and are formed with little energy requirements at ambient temperatures. With just a small palette to paint from, it is able to achieve an astonishing range of structures and functions where evolution and natural selection are the mechanisms that filter out the bad designs. Nature has developed ways to interface soft and hard materials with far superior capabilities than currently we have. Their sensing systems are extremely sensitive and only limited by quantum effects [401, 402] and as we will see many biological materials have mechanical properties far surpassing those of the bulk materials they are composed of, something not so common with engineering material systems. Nature has seamlessly integrated multifunctionality into its materials and structures something we're only now about to start.

From an economic point of view, the US's Fermanian Business & Economic Institute have estimated how the field of biomimicry could account for 1.6 million US jobs and $1.0 trillion US GDP in 2025 [403].

Lepora et al. [404] performed a statistical survey of biomimetics field in engineering and related sciences and discovered how this field had been doubling in size every 2–3 years, which outpaced general science's expansion of 6% per year. Until more recently, the increase in number of papers can be seen in **Fig. 81 b**. A lot of the interest is related to materials as many of the publications are in journals concerning material research (**Fig. 81 a**).

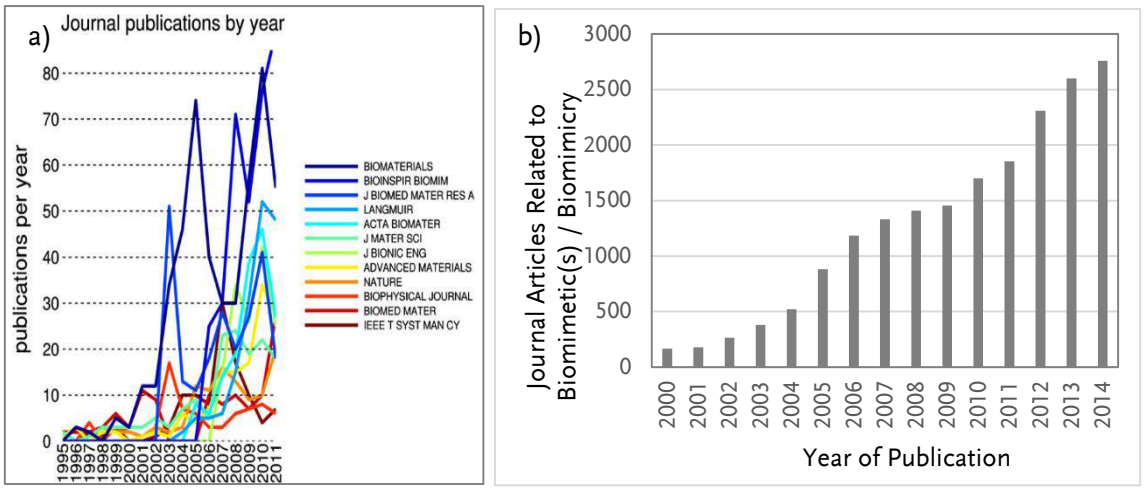


Fig. 81 – a) Number of papers published related to biomimetics for the specified journals [404]; b) Literature survey on journal articles containing Biomimetic(s)/biomimicry in the title, data from EngineeringVillage.com in June 2015.

From an engineering point of view, the understanding of the mechanical behavior of natural materials inspires and gives us new strategies and guidelines to design more advanced materials. Jamal et al. [405] found in some tests how by being exposed to biological examples, afterwards the subjects increased the novelty while maintaining variety of the generated ideas. This relatively new subject of biomimetics which includes, among others, bio-inspired materials has seen an increasing interest in scientific communities.

While many things were indeed bioinspired like Velcro, some self-healing mechanisms, EAPs and SMPs fibers for actuation, others aren't so clear such as the photographic camera and the honeycomb. Yet, since their underlying working principle is the same or so similar, they could have been.

We now discuss three important concepts that nature has been using very successfully and which are responsible for many of natural material systems incredible properties.

On Multiscales, Hierarchy and Surface Utilization

Nature uses these 3 concepts beautifully well and only now are we starting to use and see their immense importance.

As mentioned in Chapter 2.2, multi-scale composites are those that exhibit structures at different scales of length, for example, a carbon or glass fiber and CNT reinforced matrix. If these structures are organized so that lower scales' structures form the higher scales', then they are called hierarchical structures, which is what constitutes many natural materials such as bamboo, bone [406], spider and other insects silk, and many more, some of which will be shown here.

Both multiscalability and hierarchy can play a role in determining the bulk material properties. Understanding these effects can aid in the development of new materials with properties tailored for specific applications.

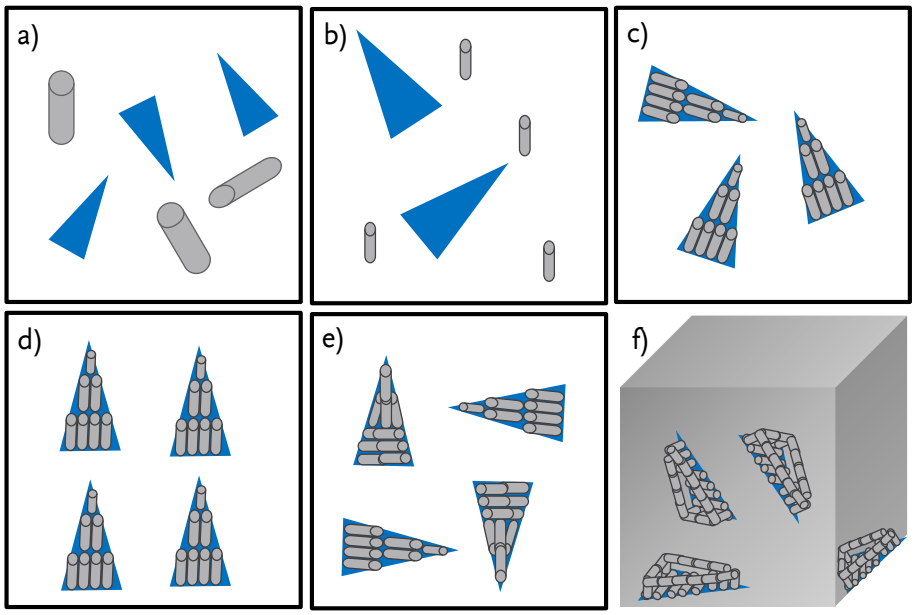


Fig. 82 – a) Composite; b) Multi-scale composite; c) Hierarchical composite/structure; d) 1D hierarchical composite; e) 2D hierarchical composite; f) 3D hierarchical composite.

The multiscale property can be double-scale or of 2nd order if structures are present on 2 different scales, tripe-scales or 3rd order if structures are present on 3 different scales, and so on. Depending on the number of axis necessary to describe the structure, it can be one, two or three dimensional (**Fig. 82**).

Lakes [407] has revealed some usefulness in studying multiscale materials by showing how high order honeycombs and foams can have greater strength and toughness than their lower order counterparts. The hexactinellid sponge *Euplectella aspergillum* that Joanna Aizenberg and colleagues studied [408] reveals 6 hierarchical levels from meso- to nanoscale (**Fig. 83 a-c**). Bone is also an example where each level has a different kind of material (fibrous, laminar, porous and particulate) that is responsible for a different property that bone possesses, for example the collagen fibers are responsible for the stiffness (**Fig. 83 d**). By looking at the cross section of feathers we initially see a honeycomb structure at the microscale. But then zooming to the nanoscale we observe that each of the membranes that constitute de cells of the internal layer are made of fibers (**Fig. 83 e**).

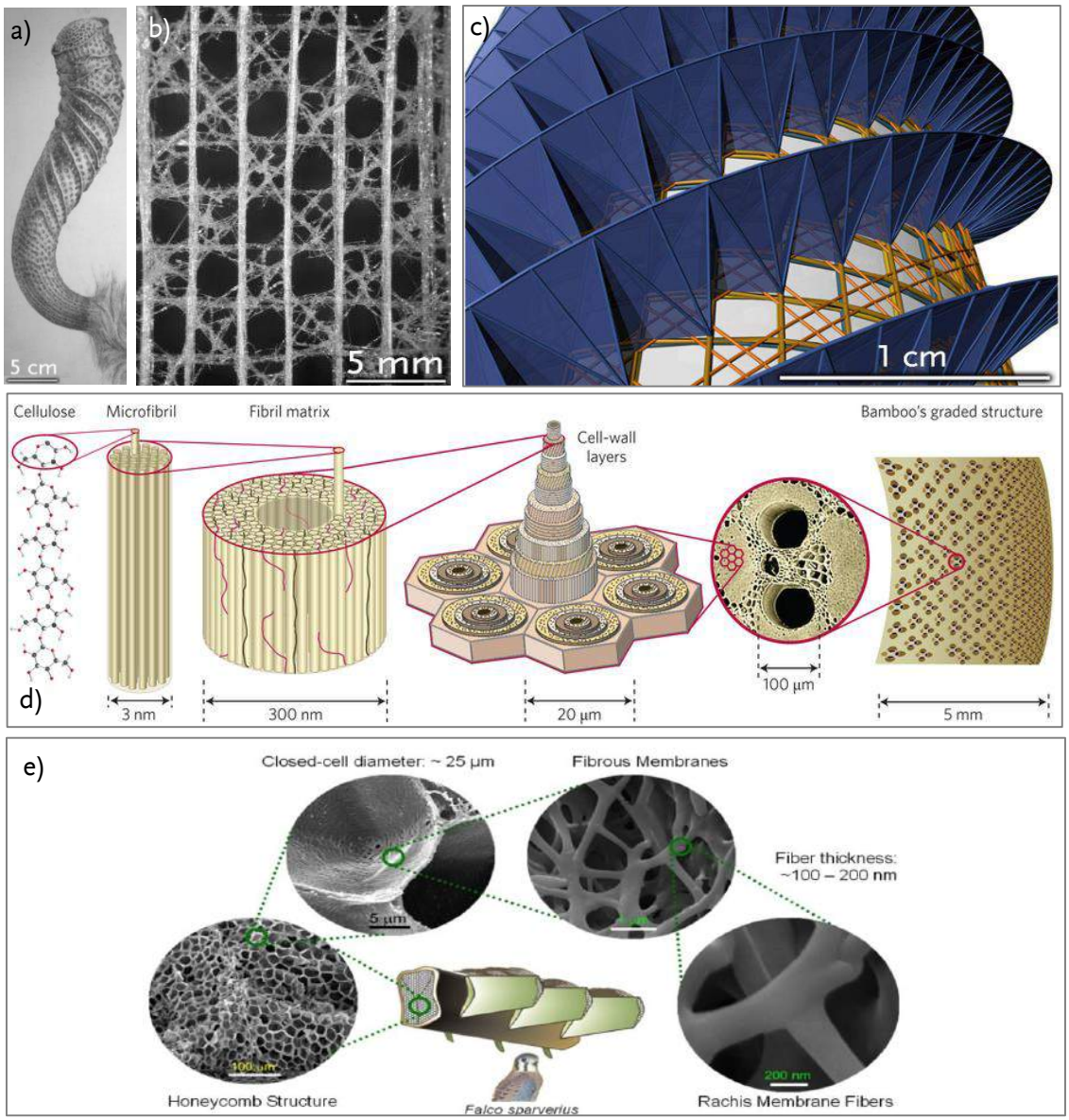


Fig. 83 – a) Skeleton of the *Euplectella aspergillum*; b) The ordered square-grid arrangement of the skeletal lattice; c) Rendering of the skeletal structure [408]; d) Schematic drawing of the bamboo's hierarchical structure [382]; e) SEM micrographs and drawings of the hierarchical structure of falcon feathers.[409].

Lotus leaves possess air trapping mechanisms at micro scale by papillae and at the nano scale by wax tubulus (**Fig. 84 a-e**). Due to the nanoscale size of these protruding structures it also achieves a self-cleaning mechanism since the contaminations are usually bigger, and therefore rest on their surface and get carried away with water droplets (**Fig. 84 o**) [410]. Pitcher plants possess fibrous nanofilaments where in wet conditions a thin water film forms on their surface promoting hydroplanning making insects and animals to slide inside (**Fig. 84 l-n**) [411]. The hierarchical structure on the water striders' legs give them super water repellency allowing it to support itself on water.

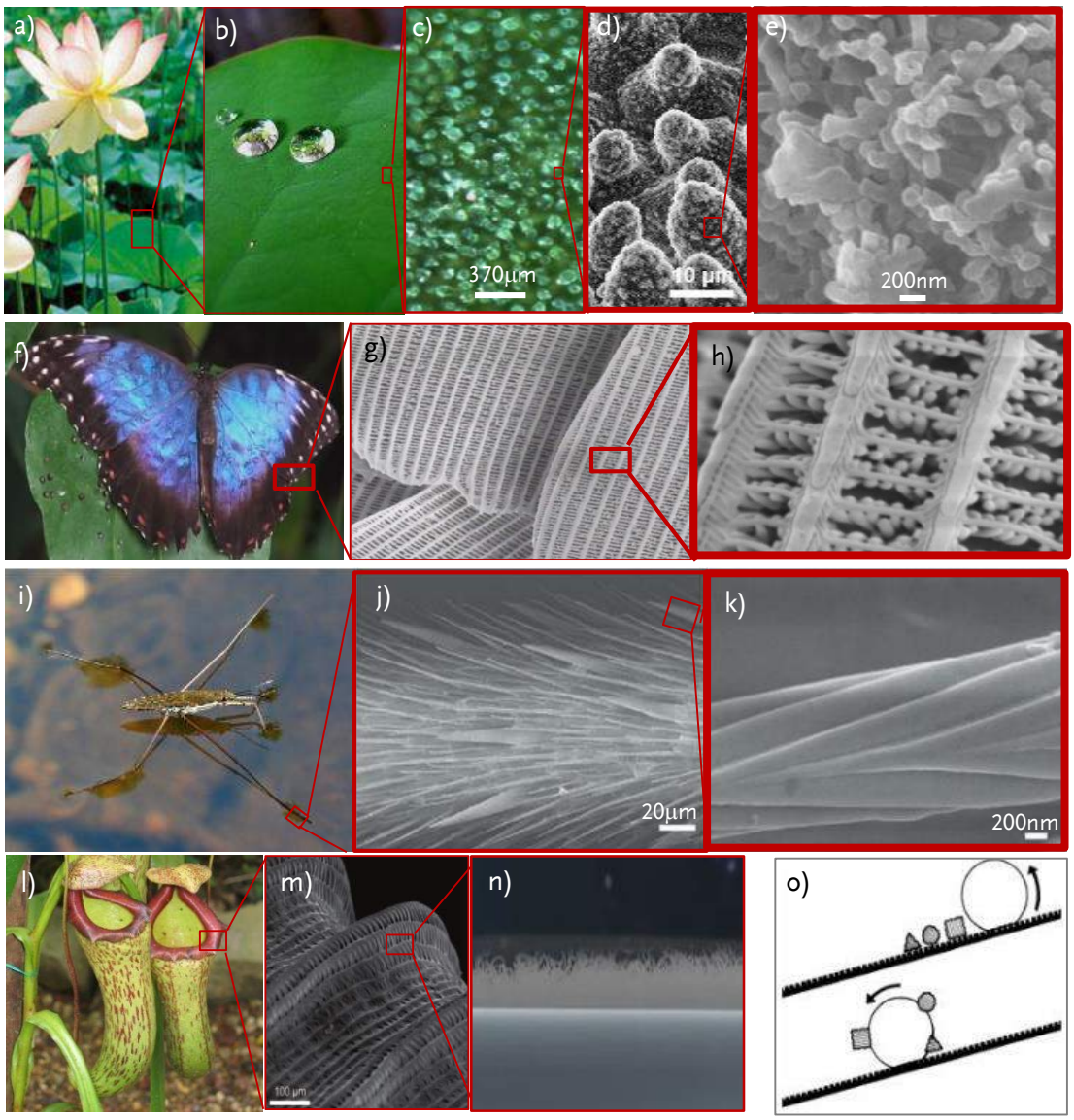


Fig. 84 – Two examples of nature's way of achieving slipperiness **a)** Lotus flower [411]; **b)** Lotus leaf[412]; **c)** Rough texture of the lotus leaf at the microscale that conveys the lotus leaf hydrophobicity; **d)–e)** Protruding nano-structures (papillae) that trap air in their midst allowing a high surface tension to develop between surface and water droplets creating *super*-hydrophobicity [413]; **f)–h)** Structures responsible for the colored appearance of butterflies [412]; **i)** A water strider resting on water surface ; **j)** SEM image of a water strider's leg revealing oriented needle-like protrusions (microsetae) which in turn have a **k)** grooved structure [412]; **l)** Pitcher Plants [414]; **m)** SEM micrograph of ridges in the rim of the pitcher plant [415]; **n)** Waxy tubules present on the ridges, trapping a thin water layer on the surface which promotes hydroplaning [416]; **o)** Schematic of self-cleaning mechanism in Lotus' leaves [411];

The iridescent color of butterflies doesn't come from pigments on the skin but due to the way light scatters when hitting the textured surface of its wings, a property called structural color (**Fig. 84 f-h**).

There are some man-made macro structures that exhibit some degrees of hierarchy. One very well-known example is Eiffel's Tower which is of 3rd order and has a density over one thousand times lower than wrought iron, the material it is made of (**Fig. 85**).



Fig. 85 – a) Eiffel Tower seen from *champ de Mars*, Paris, France. b) detail of one of the legs revealing the intricate hierarchical structure [417].

Some preliminary works in developing composites of hierarchical nature are also already underway. For example, the reinforcing of CFs with CNTs which in turn will reinforce a matrix is being studied [418]. The reinforced CFs showed increased mechanical properties comparatively to the pure version (37% increase in tensile strength and 48% in Young's modulus), and it possible that the CFs reveal new functionalities due to the embedded CNTs.

Another more systematic approach also being followed is to create hierarchical structures from the ground up such as micro- and nanolattices. Julia Greer and her colleagues are lead scientists on the subject and have recently published an example of a successful attempt of creating an alumina nanolattice of the octet-truss type (**Fig. 86 a**) [419]. It showed vastly improved toughness (**Fig. 86 b**). By taking the structure to the nanometer level, it is possible to create materials with less flaws, closer to being ideal materials. This way it was possible for the material to take advantage of the shell buckling deformation that happens instead of fracture for low thickness-to-diameter ratio of the struts. In some of the tests to 50% strain compression, some of the lattices with the smallest wall thicknesses (5-10nm) were able to recover to 95% of their initial size. Other tests made by the same authors in several other spatial configurations and materials observed a marked increase in specific strength of the nanolattices comparatively to bulk materials (**Fig. 86 c**). The high specific strength also means that these materials have a high structural efficiency, meaning they use fewer materials to reach the same strength. The current main issue is mass production since the nanolattice was manufactured by photoligography, and the whole structure is about half the size of the diameter of a hair (**Fig. 8**).

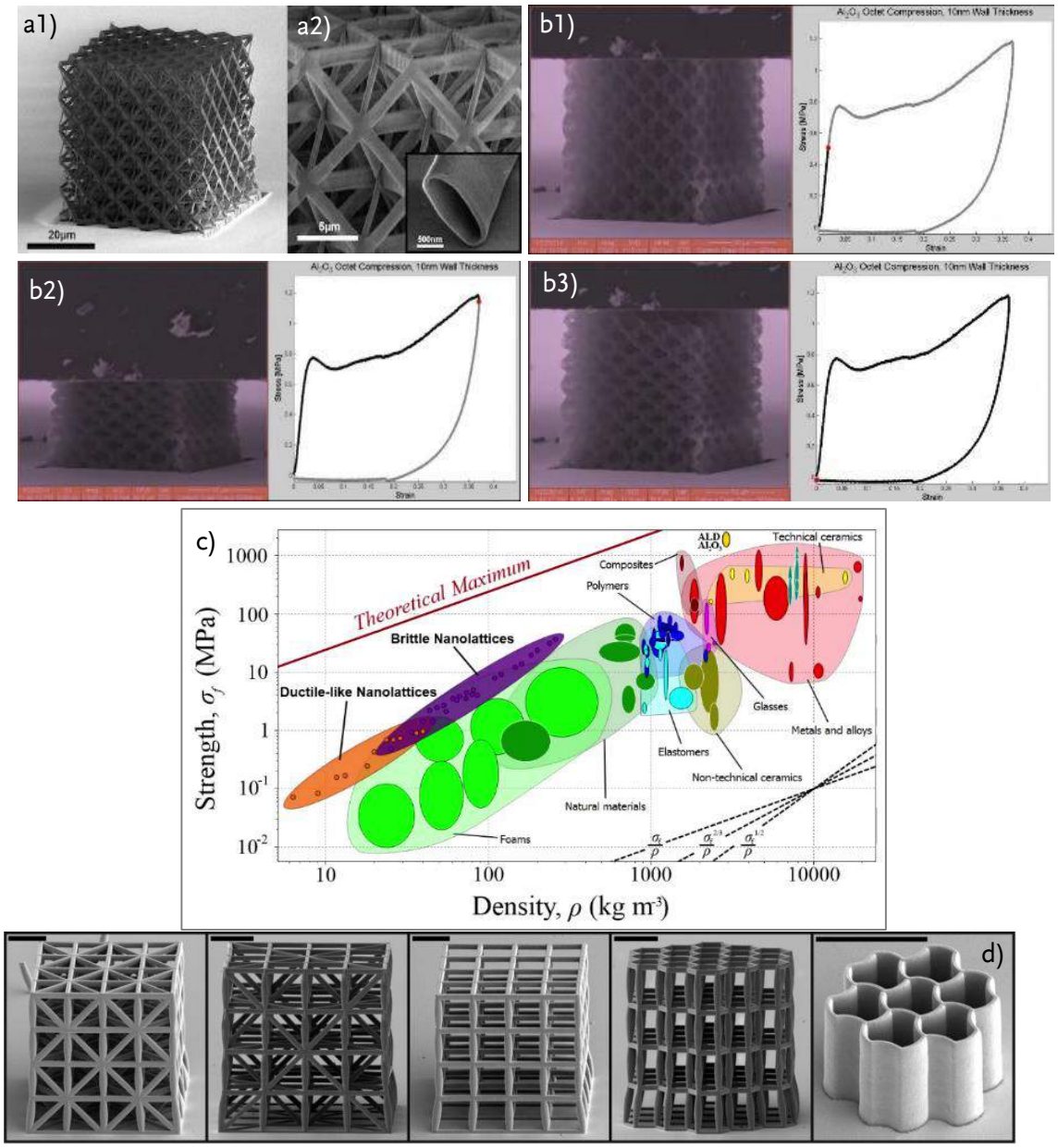


Fig. 86 – a) An alumina octet-truss nanolattice; b) Compression test revealing vastly improved toughness [419]; c) An plot of strength vs density revealing the higher specific strength of the nanolattices produces by Greer and colleagues [420]; d) SEM micrographs of other examined microarchitectures (scale bars: 10μm)[31].

For hierarchical materials to be useful, the weight savings need to surpass the cost and added complexity of multiscale manufacturing. The resulting structure must also be manufactured with very good precision, because they are more sensitive to imperfections, as an error in the lattice may bring a falling dominoes effect because of how the stress propagation must be carried out for the structure to properly function.

The last topic for this chapter concerns the usefulness in adding functions to the skin of structures. Traditionally, the surface of engineering materials is mentioned when talking about concerns for the developing of cracks, stress concentrations, roughness and tolerances and not so much as a way to add new functions to the material/product. However,

it indeed can be engineered to achieve desired functions, and we are increasingly seeing it.

The examples on **Fig. 84** also show how ubiquitous the presence of added functionalities to living beings' skins is. One of the constraints living organisms abide by is low energy availability, which results in them being extremely energy efficient. One way to increase efficiency is precisely to combine as many mechanisms and functions in the same structure, and a good example of such a structure is skin. Because organisms interact with the environment they live in, we can almost always find in their skins some form of multifunctionality.

A Few Other Examples of Inspiring Natural Materials and Structures

All of the material systems mentioned before are inspiring and can give rise to new technologies. In this chapter, other material systems that haven't been mentioned in any of the previous chapters but are nonetheless very interesting, are presented.

Spider Silk

Spider silk is a protein fiber spun by spiders. Even though the atomic interactions (mainly hydrogen bonds, which are the basic bonds that hold proteins together) are up to 1000 times weaker than those in steel or the covalent bonds in Kevlar, it manages to have great mechanical properties (**Table 9**) due to its hierarchical nature (**Fig. 87**).

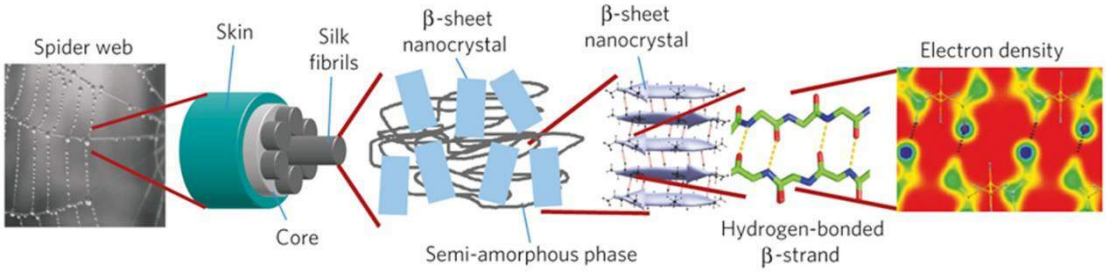


Fig. 87 – Hierarchical structure of spider silk [421].

Table 9 –Average mechanical properties of natural and synthetic fibers and a high strength steel, adapted from [422, 423].

Material	*ρ (kg/m³)*	*E (GPa)*	*σ_u (MPa)*	*ε (%)*	*Toughness (MJ/m³)*
MA silk	1300	10	1100	27	180
Silkworm silk	1300	7	600	18	70
Nylon 6.6	1100	3	950	18	80
Kevlar 49	1400	130	3600	2.7	50
Carbon Fiber	1800	300	4000	1.3	25
Steel	7800	200	1500	0.8	6

MA silk = produced from major ampullate (glands) from spiders

Silk has served both as an inspiration for artificial fibers [424] and has a pillar for other materials to develop. For example, Lepore et al. [425] reported the production of graphene/CNTs-incorporated spider silk measuring a Young's modulus of up to ~47.8GPa, a fracture strength of up to ~5.4GPa and the highest ever recorded toughness

modulus of up to 2.1 GJ/m^3. This was achieved by spraying the spiders with aqueous dispersions of graphene and CNTs.

A question then arises, can(/should) this be tried on other biological materials?

Limpets' teeth

Recently another biological material has also come to scientists attention for its superb mechanical properties, the limpets' teeth. It has a tensile strength of 4900±1900 MPa and Young's Modulus of 120±30 GPa [426]. For comparison, high-performance Toray T1000G carbonfibres have a tensile strength of 6500 MPa.

These very high values are attributed to the high mineral volume of goethite nanofibers that reinforce the soft material, whose diameters are inferior to critical size below which defects are minimal, meaning that they approach the materials theoretical tensile strength.

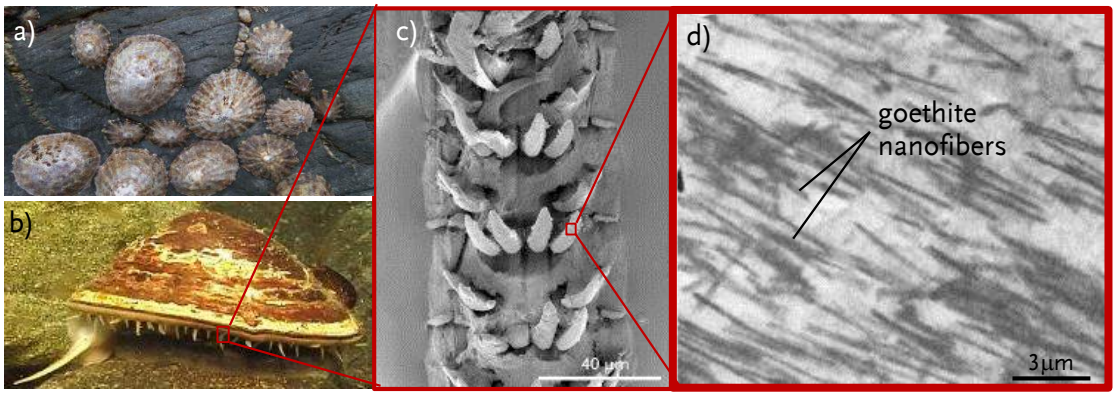


Fig. 88 – a) A family of limpets on a rock [427]; b) A moving limpet [428]; c) Detail of a limpet's leg[429]; d) Detail of a limpet's teeth showing the high anisotropy of the composite due to the high alignment of goethite (FeO(OH)) nanofibers [426].

Hagfish Fibers

Hagfish, a 400 million old fish species, have the ability of producing surprisingly high quantities of slime as a defense mechanism (**Fig. 89 a**). This slime contains structural fibers that bind the mucus sheet where a large volume of water is trapped and it is formed, through mechanisms still unknown [430], when leaving small vesicles inside the hagfish. The structural fibers are similar in size to spider threads but they are built in cells from intermediate filament proteins via a self-assembly hierarchical process. On the other hand, the spiders' threads are built from a spinning process that transforms spider silk liquid proteins into an insoluble fiber. At 800MPa of tensile strength they're not as strong as MA spider silk, but still worth looking into as the underlying principle through which it achieves such strength might be useful for developing ultra-resistant fibers [431].

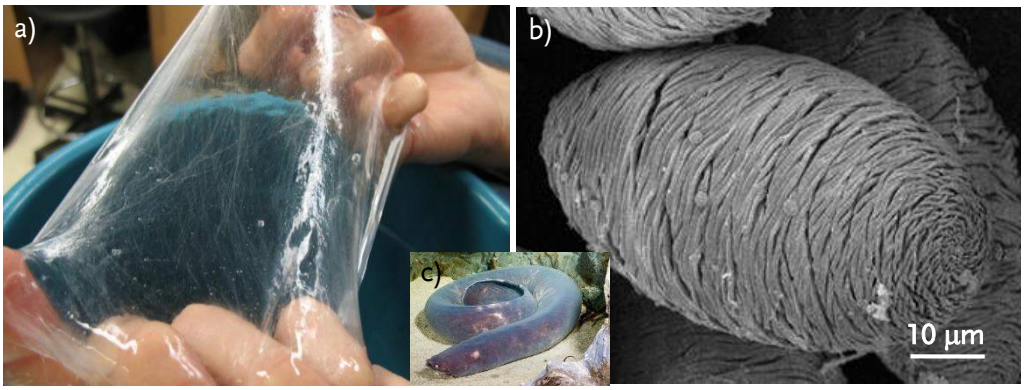


Fig. 89 – a) Hagfish slime. The threads that can be seen as very thin filaments; b) Tightly wound fiber cells as a means of storing the threads before deployment; c) Hagfish [432].

Other

Owl's Feathers

Many owls have the ability to fly with an incredibly high degree of stealth, very useful to catch their preys by surprise, due to the low sound volume they produce when flying. What allows this reduction in noise seems to be a combination of different feather structures in the leading and trailing edges of the wings, as well as a forest-canopy-like structure of the feathers.

Inspired by that structure, some researchers have recently created a material that when covering the underlying structure was able to significantly (up to 30dB) reduce the noise produced [433].

Shark's skin – It is > 80% v/v collagen which has a rupture strain of 4%. However when swimming from side to side the skin expands and contracts 10-15% and 1-15% respectively. This is allowed by the crossed-helical array of fibers, resembling a 45/-45 layup wrapped around a cylinder. Not only that but to bear the increased stress and to allow a better force transition from the muscles when swimming at high speeds, it has the ability of changing its stiffness by a factor of 13 [434]. This is in addition to the drag reduction functionality that it exhibits and will be further explored in the next chapter.

Plants and trees – There could be valuable actuation lessons to be learned by understanding how mimosas and sensitive fern bend their leaves when touched, or how bug-eating plants closes themselves around the bugs or how the sunflower changes it's flower orientation in the sun's direction throughout the day to maximize its exposure to light. Since all of these actuations are embedded within the same material that both supports the plant and provides it with energy harvesting through photosynthesis, they are truly multifunctional materials. Another way, along with hierarchical structure, that trees use to increase structural efficiency is stiffness variability which can occur [435]:

- Due to moisture and temperature changes (glass transition);
- Cross links and sacrificial bonds;

- Across one scale;
- Across many scales (hierarchical structures).

Next, some case studies are discussed of natural material systems, the extraction of the underlying principle that enables the desired function, and its application to an engineering material system.

Case Studies of Bio-inspired Material Systems

Adhesiveness – Geckos' feet

Geckos' are known for their ability to climb surfaces with apparent ease, and without their feet having any kind of adhesive substance. It was discovered that they have an intricate hierarchical structure (**Fig. 90**) that ultimately result in a huge surface area at the nanoscale which allows van der Waals forces to generate between the gecko's feet and the surface which are responsible for the adhesion mechanism. This adhesion is directional, for it to work, the gecko needs to put its paws in a certain direction and then slightly drag it, so that all the multiscale structures work in the same direction. The underlying principle to be extracted from this is

P1) An anisotropic hierarchical structure that has a very high surface area which generates van der Waals forces.

Cutkosky [436] created a silicon rubber structure based on just that (**Fig. 91 a-d**) and applied it to a robot gecko to demonstrate its functionality (**Fig. 91 e**). Even more recently, it was discovered that geckos also use electro-static forces to generate even more adhesion power in surfaces where such is possible [437]. This resulted, when applied to the climbing robots, to some impressive feats such as a 12 gram robot pulling 24kg, which would be roughly the equivalent of a human being pulling a blue whale.

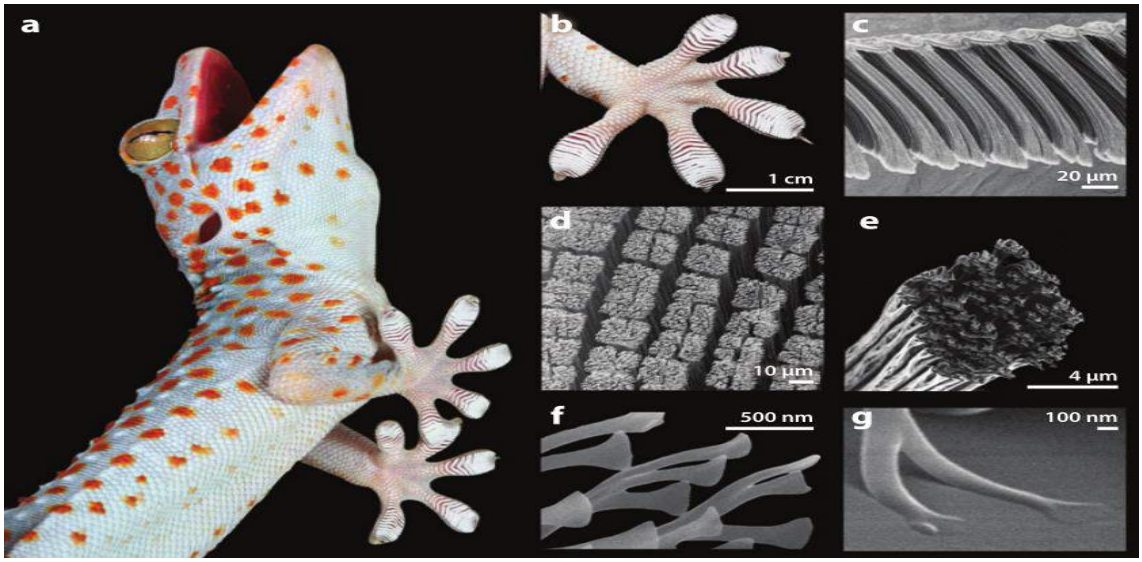


Fig. 90 – Structural hierarchy of the gecko's adhesive system at increasingly smaller scales from a) to g) [438].

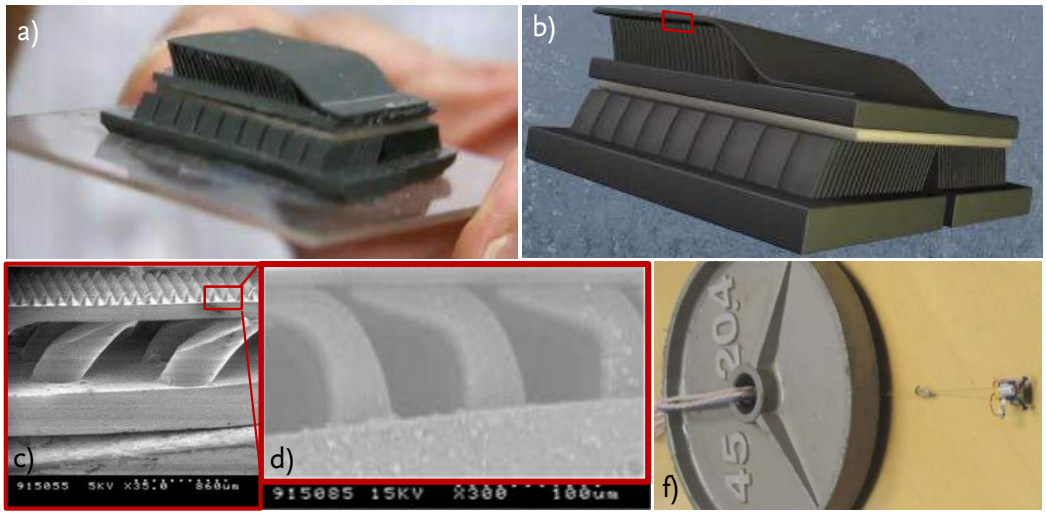


Fig. 91 – a) Prototype of silicone rubber bio-inspired directionally adhesive structure [412]; b) 3D render of the prototype [412]; c) SEM micrograph of a detail of the top part of the hierarchical structure [439]; d) SEM micrograph of the terminal shape on the loaded state [439]; e) The 12g μTug robot that can carry 2000 times its weight [440].

Hydrophobicity and Slipperiness – Lotus' Leaves and Pitcher Plants

The understanding of the underlying principles behind the superhydrophobicity (contact angle >150°) and hydroaffinity of these two plants has led to the production of new materials with a functional superficial structure. These are two great examples of bio-inspired designs.

Lotus' leaves – Lotus' leaves have an hierarchical structure presented in the previous chapter composed of papillae at the micro scale and wax tubules on the surface of the papillae at the nanoscale, that create superhydrophobicity (**Fig. 92 a**). The reason lotus' leaves are more frequently mentioned than other superhydrophobic species' surfaces is because they have been compared before and lotus leaves' have been shown to be consistently superior [410]. For here we're only interested in the microscale papillae (**Fig. 92 b**), which trap air in their midst not allowing water to fill those spaces unless a certain critical pressure is achieved (**Fig. 92 c**). The underlying principle behind this function is then:

P1) Presence of cylindrical/conical sub-micro structures that protrude from the surface which trap air in-between maintaining the surface dry.

Checco et al. [30] produced a super hydrophobic surface by, among other steps, etching the surface of a substrate of silicon, leaving it with cylindrical or conical pillars (**Fig. 92 b-c**. The size of the pillars is modestly lower than that of the papillae and the reasons are to increase the robustness of water repellency, something that in the papillae is done by their waxy tubules.

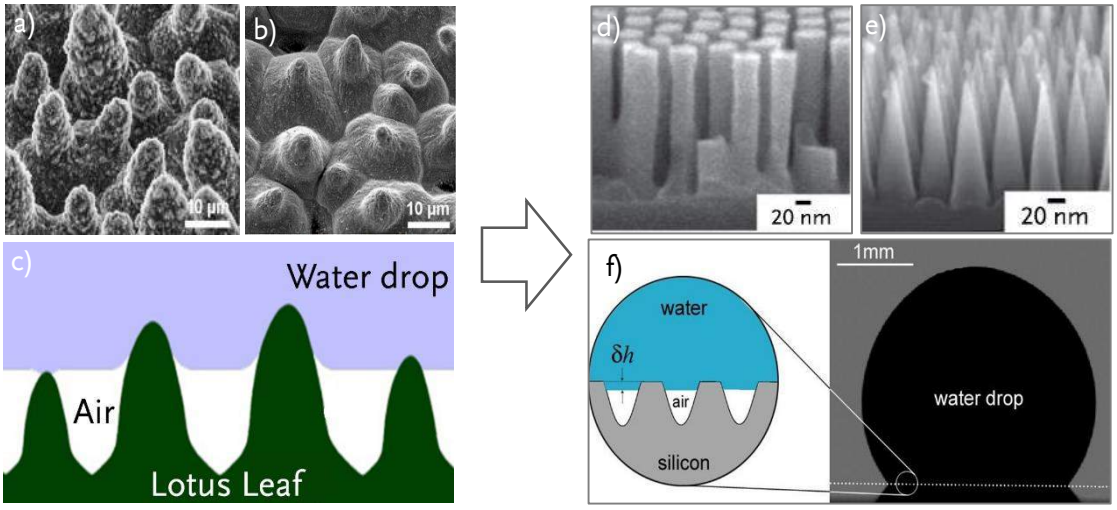


Fig. 92 – a) Papillae of a lotus leaf; b) Papillae after the removal of the wax tubules; c) Schematic explanation of the underlying principle [410]; SEM micrograph of a silicon surface textured with d) nano cylinders and e) nano cones [30]; f) Illustration of the underlying principle applying to the synthetic material (silicon)[441].

Pitcher Plant – The rim of this plant (named peristome) has a regular microstructure with radial ridges and an anisotropy of topography directed towards the inside of the plant. In the rim, and at the nanoscale, there are bundled nanofibers that trap humidity, water rain and nectar secreted at the inner margin of the peristome, creating a thin liquid film at the surface. This combination of anisotropic surface and aquaplaning promoting surface are the two mechanisms responsible for the slipperiness of the rim and the demise of the insects that dare walk on top of it. The underlying principles are:

P1) Anisotropic surface topography in the direction of the sliding movement;

P2) Liquid filled and trapping bundles of fibers that are able to create a thin film of the trapped liquid.
P1) depends on P2) because if the surface isn't wet, the dry surface has too much adhesion.

In creating SLIPS™ [442] **P2)** was applied (**Fig. 92 d**) by using arrays of nanoposts and bundles of Teflon® fibers and a lubricating film (**Fig. 92 e-f**) both revealing very high liquid repellency.

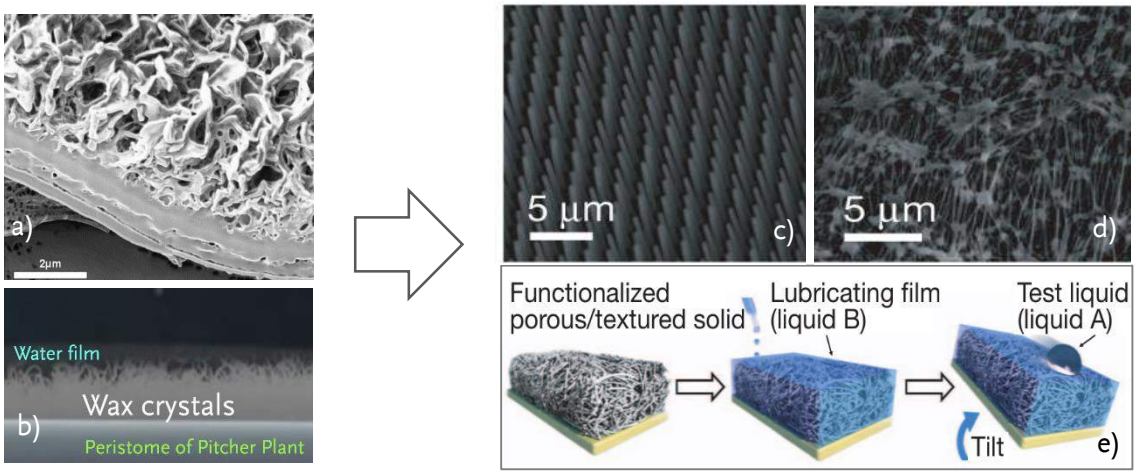


Fig. 93 – a) SEM micrograph of the wax crystals on the peristome of a pitcher plant[443]; b) Underlying principle of the slipperiness of the rim of the pitcher plant (adapted from [416]); SEM micrographs of two configurations tested: c) arrays of nanotubes and d) randomly distributed Teflon nanofibers e) Application of the underlying principle behind the slippery surface of pitcher plants into a synthetic material [442].

Drag Reduction and Anti-biofouling – Shark skin

Despite fish being constantly at sea, unlike moving boats, they don't gather as much algae and bacteria on their skin. Sharks skin is reportedly one of the best at this and it impedes bacterial growth because the distinct ridges on its diamond shaped scales' surface are so small that bacteria need to expend extra energy to suspend over those gaps. When moving, the stress on the bacteria's cells attachments increases even further and with it, the effectiveness of the anti-biofouling [444]. It is unclear whether the diamond shape is simply coincidental of the positioning of the denticles on top of each other or if they are also unfavorable to biofouling. Also the small vertical gaps between the denticles might also be responsible for a part of anti-biofouling since other fish, despite not with the same efficacy, also present this property [445]. Just in case, it will be included in the underlying principle which would then be:

P1) Ridges of sub-micron size or size that best reduces bacteria attachment aligned in the flow direction and forming among them diamond shapes.

Sharklet Technologies® [446] has this principle applied in their antifoul plastic sheet product (**Fig. 94 c**). The vertical drop between denticles has been replaced with horizontal space while maintaining the diamond shape.

Also of interest about the shark skin, is the swimming efficiency it provides its bearer. The same ridged surface lifts and reduces turbulent vortices size when the sharks are swimming, thereby reducing overall drag (**Fig. 94 b**) [445].

The drag reduction functionality was mimicked by Wen et al. [447] by 3D printing thousands of small (1.5mm) plastic denticles and putting them on top of a flexible membrane. The 3D shape of the denticles was obtained by using micro-CT imaging of the skin of a shark species (**Fig. 94 d**).

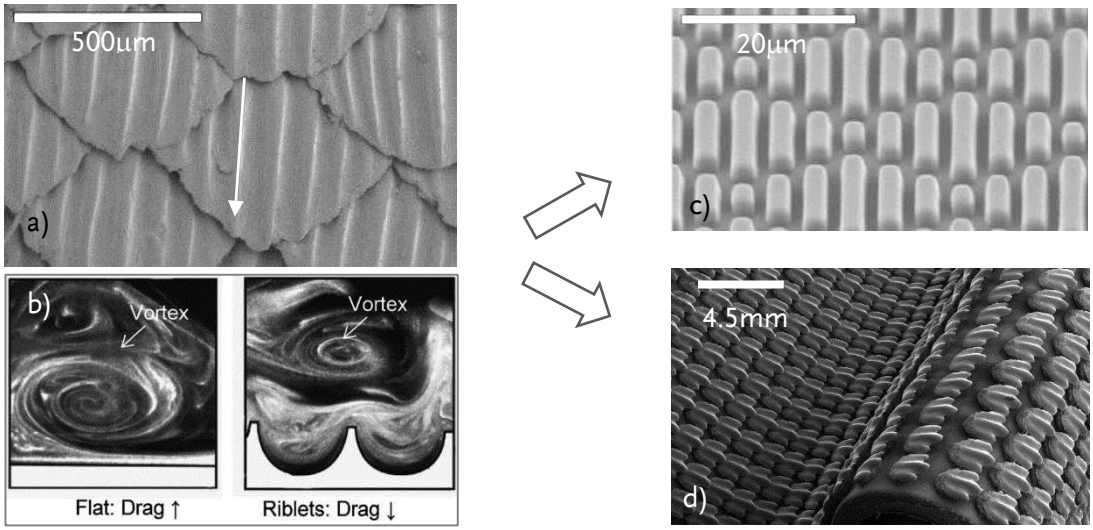


Fig. 94 – a) Shark skin revealing dermal denticles that are one of the responsible for high swimming efficiency of sharks. Arrow indicates flow direction; b) Reduction of drag through lifting and reducing of size of turbulent vortices. Flow into the page.[445]; c) Sharklet™ synthetic surface with antibiofouling properties [446]; d) SEM micrograph of 3D printed plastic denticles to reduce a surface's drag[447].

Now Lufthansa [448], Airbus [449] and university researchers [450, 451] are studying how to apply it to commercial aircrafts in order to decrease drag and increase fuel savings.

Self-healing – Mammal skin

In mammals, when a cut is made on the skin and superficial capillaries are ruptured, the blood that was circulating inside them now goes towards the surface. The contact of the blood with the air triggers a chain reaction resulting in platelets rushing to the cut and the production of fibrin that holds blood cells tightly together in a bundle, stopping further blood to flow to that place (**Fig. 95 a**). The underlying principles are

1) That contact between a part of the material system and air triggers the healing mechanism, and that a fracture results in said contact;
2) The first step in the healing process is the filling of the fracture by products of the reaction of the system with air.

Mammals prevent any reaction to occur before the rupture, by the presence of a skin and the sealing of the "healing agents" inside the circulating blood, isolated from air.

Tavangarian et al. [325] created a healing mechanism with the same underlying principles. A SiC/spinel nanocomposite is put below a thermal barrier coating. When that coating is ruptured due to a fracture, SiC reacts with the oxygen in the air, resulting in a 80% in volume expansion of the reacting zone due to the formed SiO_2 80%. This silica further reacts with the spinel resulting in mullite which has a binding effect (**Fig. 95 b-e**).

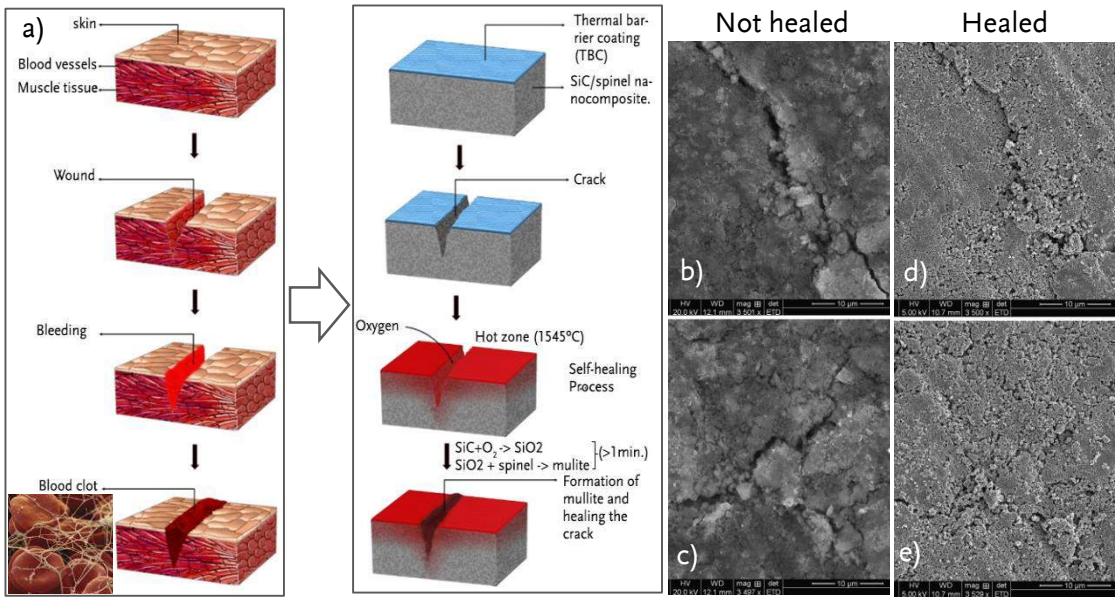


Fig. 95 – a) Comparison of biological healing to the self-crack healing mechanism, the inset is a colored SEM micrograph of a blood clot revealing platelets, erythrocytes and fibrin; Various cracks b)-c) before and d)-e) after sintering in air for 1h [325] (all images adapted).

Color change – celaphopod's and chameleon's skins

Celaphopods and chameleons have a somewhat similar mechanism for their color change ability. Their nervous systems contracts or relaxes cells in the skin depending on the color they want to portray.

Octopus' skin – One of the most studied celaphopods' color change abilities are the octopi. These have a property called metachrosis, where chromatic change results from the expansion of certain pigment cells (**Fig. 96 a**). They also are photo-responsive in the way that their nervous system automatically senses the colors of the environment and are able to translate that into the contraction of the pigment cells in order to blend in and become apparently transparent. The underlying principles are then

P1) Elements that show color depending on their strain;
P2) Photo-sensitive elements that communicate with the elements responsible for color.

In the following paragraphs 3 examples of inspired technologies that successfully incorporated at least one of the underlying principles are presented.

Ge and colleagues [452] created a thin film of elastomeric poly(dimethyl siloxane) (PDMS) embedded with silica nanoparticles. When relaxed the materials is highly transparent, but by being stretched, cracks and wrinkles appear making it opaque by diffusing light and colored depending on the nanoparticles' size [452] (**Fig. 96 c**) (P1).

Wang et al. [453] produced an electro-mechano-chemically responsive layered structure which when electrical fields are induced, patterns of deformations are formed. If sufficiently deformed it shows fluorescence (**Fig. 96 d**) (P1).

Yu et al. went further and mimicked each of the functional octopus layers (**Fig. 96 e**) [454] (P1&P2). Layers 'ac' and 'al' mimic the chromatophores, layer 'am' mimics the muscles that are responsible for the expansion and contraction of the chromatophores, and the 'ao' layer mimics the photo-responsive proteins in the squid's skin.

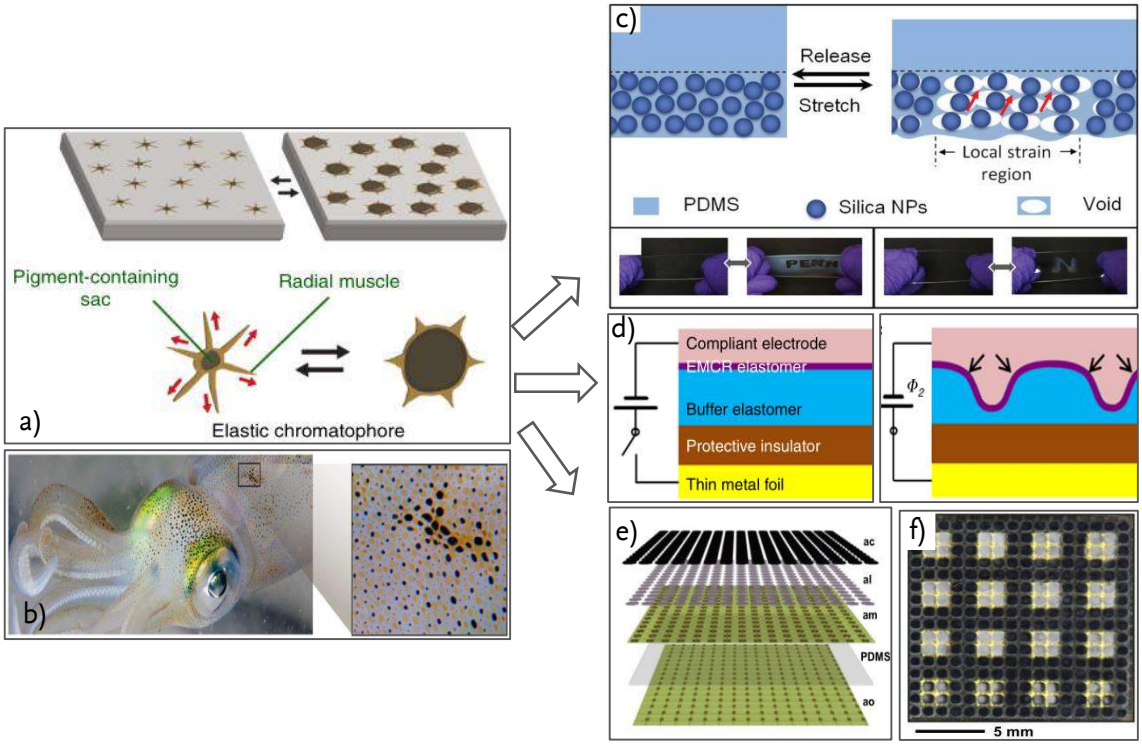


Fig. 96 – **a)** Schematic of metachrosis, the mechanism responsible for the coloration change of cel-aphopods ; **b)** Skin chromatophores of a squid [453];Three celaphopod-inspired color change mech-anisms: **c)** Mechanism of transparency change and composition of a mechano-responsive sil-ica/PDMS film [452]; **d)** Layers and the electrical actuation of an electro-mechano-chemically re-sponsive elastomer for on-demand fluorescence [453]; **e)** Layers of a celaphopod-inspired photo-responsive skin; **f)** Demonstration of a static pattern of the adaptive skin matching its background [454].

Chameleon's skin – Recently Teyssier et al. [455] fully discovered the working mecha-nism behind the chameleon's skin change of color. Chameleons have one to two layers, whose cells are named iridophores, below the epidermis that contain nanocrystals that reflect light based on the spacing between those nanocrystals. To change that spacing, and therefore color they change the salt balance of the iridophores resulting in a shrink-age or swelling of the iridophores. The working principle is then

P1) The color of the light reflected depends on size and spacing between protruding el-ements in a reflective surface.

When Zhu et al. [456] published a paper concerning a flexible strain-responsive color changing structure, that discovery was yet to be made for a few months. But still, the structure they produced uses the same working principle responsible for the color change in the chameleon's skin. The structure consists of a silicon film with an etched array of thin beams embedded into a plastic film. By stretching the structure they were

able to change its color for 39nm of wavelength from green to orange. They report that, exactly like the chameleon, the color reflected by the structure depends on the spacing between the bars and their size.

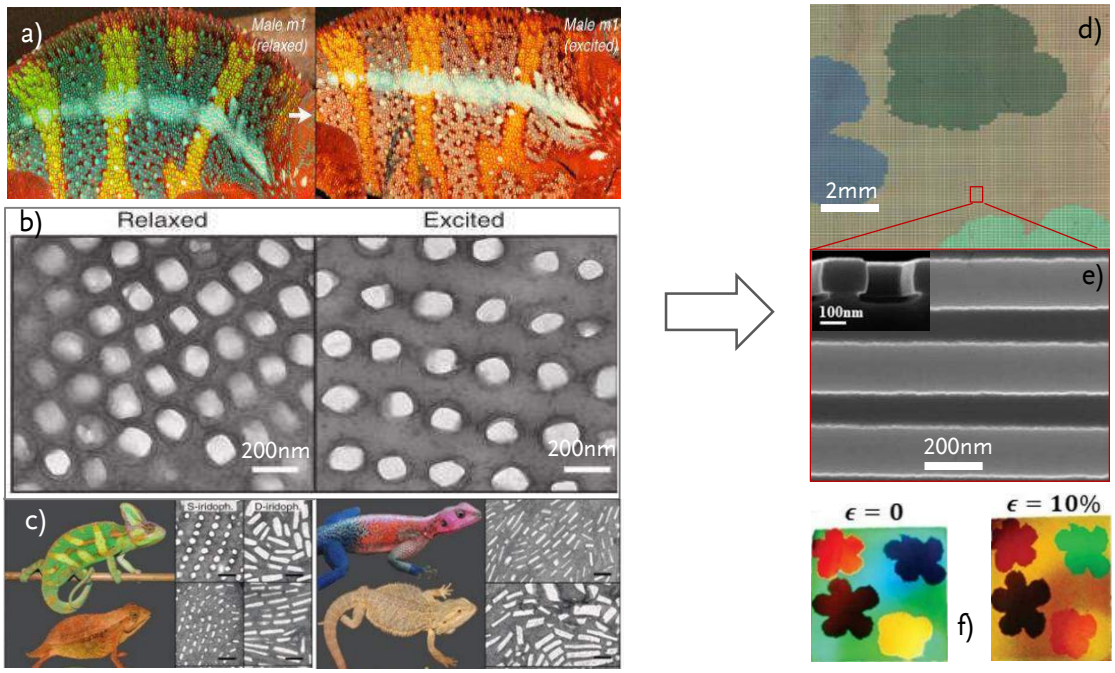


Fig. 97 – a) Color change occurring during excitation of a chameleon; b) TEM micrographs of nano-crystals in iridophores on their relaxed and excited state [455]; c) Iridophore types in lizards. The first 2 exhibit 2 superimposed layers (scale bars=500nm); d) Picture of a sample of the flexible color changing structure; e) SEM micrograph of the view from the top. The inset shows the cross section of the bars; f) Photo of the chameleon-skin-inspired changing color material with 0% and 4.9% strain[456].

Other interesting examples of biomimetics-based applications and designs have been compiled by Vincent et al.[457], Helms et al. [458] and Cohen [459].

These case studies helped in understanding the process of bioinspiration. In the following chapter, I present a few ways to perform bio-inspired innovation.

Methods for Systematic Innovation Through Biomimetics

General Principles Followed by Natural Systems

Before going any further, there are a few principles that are seen frequently in biology and that should be pointed out because they can help us to understand the general 'reasoning' behind biological designs:

1) The way nature performs a function requires the least amount of energy [460];
2) Nature builds structures using the local commonest materials;
3) Given the constraints, including the environment and the evolutionary history of the system, the systems developed are the most reliable.

The universality of these assumptions can be seen for example on the striking similarity between mammals of different continents, even though they have evolved separately for

about 200 millions of years since Pangea split, which was more than enough time for more significant attributes to have developed if they ought to.

Principle 1 tells us how nature's solutions approach ideality. Principles 2 and 3 how the solutions must be seen in the context they were created and not as isolated entities that make sense in all environments. For example, one could study the bat's or dolphin's echolocation and realize in terms of detection mechanisms, vision is most likely superior, and therefore we could quickly dismiss echolocation as useful. However by putting the mechanisms in their context, we realize that they are used at night and for small moving insects and for long distance location of prey underwater respectively. In their respective environments, these mechanism are more effective than vision.

The context of historical evolution also matters. For example, even though the horse and the cow essentially have the same diet, cows have several stomachs while horses only have one. This is only due to the fact that when the family to each cows belong emerged, they were forced to marginal habitats where food sources were scarcer, and therefore needed a higher efficiency digestive system.

Also, P2&P3 mean that since we are not bound by the same constraints as nature, the main objective of biomimetics is to extract the underlying principles from natural material systems and apply them to our broader material pallet and our own constraints, or lack of. To exemplify, many natural materials are built over a long period of time, many times too long to be practical for human processes. So that's a constraint for us. However, nature is limited to low energy sources (low temperature/energy) processes whereas we're not so much. Understanding these differences is critical to a good biomimetic process because they might change our perception of the feasibility of certain solutions, especially for engineers who might not be familiar with, for example, the time frames that take to a certain biological process to occur.

Devising a Simple Human-based Method

There are two great groups of methods of bioinspiration depending on the starting point of the process (**Fig. 98**):

- **Solution driven** where an interesting biological mechanism inspires the search for potential technological applications;
- **Problem driven**, which is the more common approach and it's where a technological problem inspires the search in the biological world for biological mechanisms that when conveniently applied, can solve it.

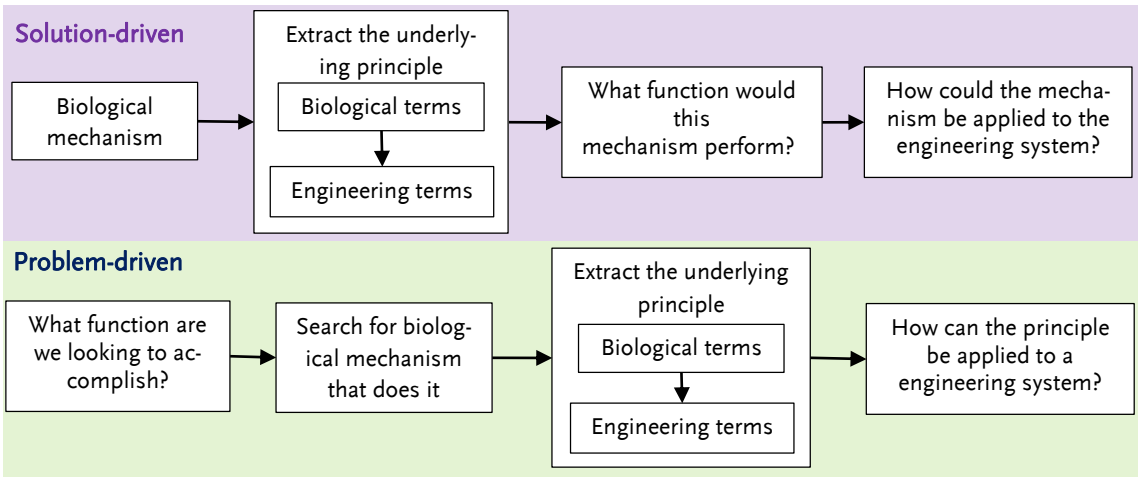


Fig. 98 – Synthesis of solution and problem-driven approaches to bioinspiration.

A Simple Problem-driven Method

In the case studies we saw the solution-driven approach being used, so now I'll present a simple systematic problem-driven approach.

1) **What function we are looking for?**
    a. Rephrasing the problem in terms of the function to obtain, simplifies the search. For example: If we intend to increase actuation force, the function to obtain is actuation. Some biological actuating mechanisms, might have low force, but the underlying principle, when applied to human technology might allow much bigger values, and a completely new actuating mechanism;
    b. By keeping the guideline broad, but just specific enough, more ideas from the natural world are allowed to pass our filters. E.g., if the problem is to obtain a more streamlined shape for a vessel, what we're actually looking for is low drag (c.f. concept fan, in subchapter Thinking Creatively);
    c. Keeping in mind the inherent multifunctionality of most biological materials. One of the reasons bone isn't stronger is because it needs to allow self-healing using the same resources the rest of the body has. Increasing system-level efficiency tends to decrease subsystems' performance. Natural systems are incredibly system-level efficient, and they pack many functions together, which can make their subsystems to appear weak, and therefore they might fly under the radar and not be studied.
    d. Functions can be (complete list in p.15):
        i. Structural, e.g. **strength**;
        ii. Drag resistance changing;
        iii. Actuation;

iv. Thermal (high thermal conductor/insulator, thermal expansion), …

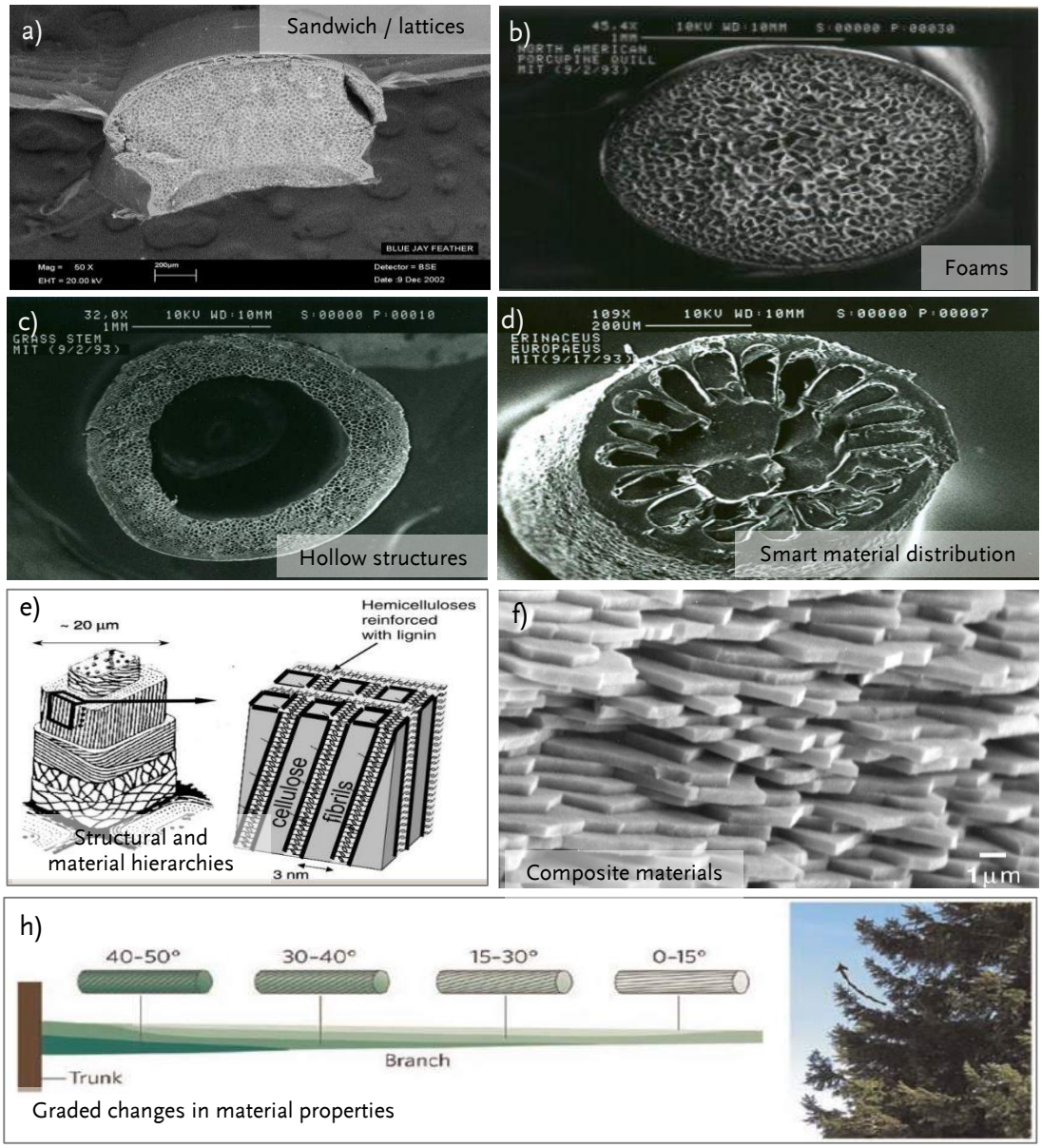


Fig. 99 – Some of natures' solutions for strength and their respective examples: a) Micrograph of a blue jay feather [461]; b) Micrograph of a porcupine quill [462]; c) Grass [461]; d) Hedgehog spine[461]; e) Hierarchical structure of the cell wall of softwood [463]; f) SEM micrograph of the cross section of a broken pearl showing the composite nature of nacre [464]; h) The orientation of cellulose fibers in a coniferous tree branch resembling a fiber reinforced polymer [435].

2) How do biological systems accomplish that function?

a. State the solutions presented by biological systems in their raw form. For strength, we'd have: wood, cellulose fibers, bone, abalone shell, animal quills, skulls (**Fig. 99**);

b. Look for extreme/specific cases. If the purpose is to increase strength, elephant bones, sequoias trunks. If the purpose is to increase specific strength, airborne animals' structures;

3) **What is/are the general/underlying principle(s) used when biological systems accomplish that function?** For strength it would be:
    a. Using composite materials;
    b. Using hierarchal organization of materials/structures;
    c. Taking advantage of size effects;
    d. Using materials smartly: honeycombs, foams, hollow structures (**Fig. 99**).
4) **How can we apply this principle to accomplish the desired function in the original system with current technology?**

Others have used similar methodologies, on which this one was based, with some success [458, 465-469]. I prefer this approach because of its simplicity and because it retains the core elements.

Artificial Intelligence's Approach

Intro

Instead of relying on the human why not outsource some of the steps to a computer software or artificial intelligence (AI)? The first obvious steps where this could be done is in searching and organizing information, but later on even entire solutions could possibly be devised by an advanced AI. This would immensely increase the productivity of doing biomimetic innovation.

We see creativity as a human process, and we've spent a great amount of time studying it in order to better understand it and take better advantage of [470]. There are those that believe machines will be capable of being creative [471, 472], myself included. In fact, AI is progressing so rapidly, that it has raised concerns about AI-safety and keeping AI-beneficial to human society of several AI researchers around the world [473].

For the past 50 years, Moore's law has proven to be uncannily accurate. And as processing power increases at such a staggering pace, so does our ability to take advantage of it. Starting this project now ensures that we can be taking full advantage of existing technology at all times and not playing catch-up.

First let's take a brief look at some of the progress that has been made in this field. There has been some work regarding automatizing certain steps of the biomimetic process. A few of the attempts are presented now.

A little bit of state of the art

AskNature (www.asknature.org) is an online library supplied by the Biomimicry Institute (www.biomimicry.net) that groups research articles about design inspired on nature by function (**Fig. 100 a**).

Chakrabarti et al. also developed a tool, SHAPPhIRE [474] to aid in inspiring designers and engineers to come up with novel solutions by providing a database of natural systems and a database of artificial systems (man-made) and their description, structure and functions (**Fig. 100 b**).

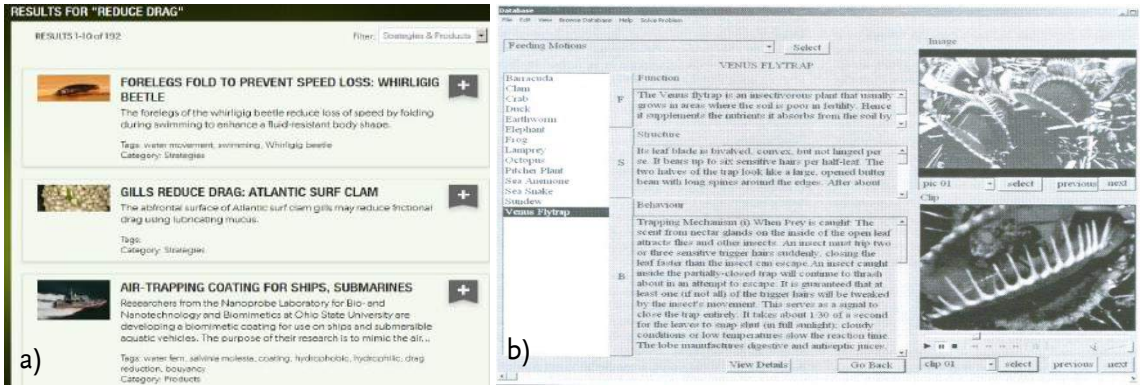


Fig. 100 – a) Searching for "reduce drag" in biological systems in www.asknature.com ; b) Original natural database of SAPPhIRE tool [474].

Bruck et al. [355] created a database of products whose design was inspired in nature responding in part to the suggestion by Cohen et al. [475] of creating a database that in addition to bio-inspired products would also include engineering analysis of biological systems.

The BioM Innovation Database [476] is a similar concept to the previous one, containing 400 bio-inspired products, with the aim of supporting research and enabling detailed case studies. Then there's also BioTRIZ [477] a TRIZ based method for bio-inspired design, and Design by Analogy to Nature Engine (DANE) [478] a design case library.

Several other studies with the same general focus in mind of an automated by computer systematizing of biomimetics have been conducted. For example Glier et al. [479] have tried text analytics methods for automated text classification for search results in bioinspired design, Vandevenne et al. [480] describe a technique of organism detection by mass reading of biology articles, Goel et al. have presented a few other examples [481] and presented a comprehensive state-of-the-art on the subject [482].

The topic of using AI for engineering design, analysis and manufacturing is a very lively field as one can see by reading some of the papers from the journal with the same name [483], and that I believe will be most, if not all, of the future way in which we design.

A Glimpse Ahead

Wilson et al. [484] found that keyword-based retrieval searches often suffer from providing too many irrelevant results. Because they're search-oriented, they also lack organizational abilities between concepts. ThinkMap's Visual Thesaurus reveals how an early stage organizational concept map looks like **Fig. 101**. If it could be possible to adapt and improve such a system to biomimetics it would greatly aid in the search for relevant biological analogies or solutions.

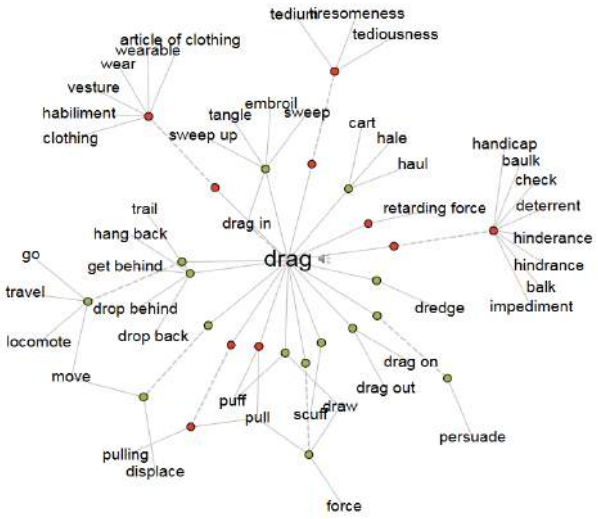


Fig. 101 – An interactive word map generated by Thinkmap's ® Visual Thesaurus® [485].

At this stage it matters to mention Wolfram|Alpha and IBM's Watson.

Wolfram Alpha is an online answer engine that provides an answer to a query by computing the **structured data** the system contains that answers the query. Comparatively, a search engine simply provides a list of links which then give access to the contents that contain the keywords searched, or in more advanced cases, links that can contain the answer, but it doesn't provide the answer itself. IBM's Watson, is a form of a more advanced search engine which recently won some Jeopardy contests against champions, where it had to understand language, puns, humor, and even learn and adapt in real time. If instead it was fed biological and artificial system's functions and asked to find patterns and predict solutions it would likely yield very interesting results. **Fig. 102** shows a comparative illustration between the 3 engines.

With the increasing rate of evolving technology and discoveries, in a not too distant future, by the time reviews about a topic are published, the state-of-the-art will already by outdated, which means that the current method of gathering information will soon need to be updated.

The ideal would indeed be to have the biological entities and the engineering concepts as structured data, so that a software understands the concepts. **Fig. 103** shows a simple ontology related to wood composition showing how the concept understanding of a machine would look like. The process of machine learning would be akin to baby human learning, continuously acknowledging 'what' is something and how it relates to other things.

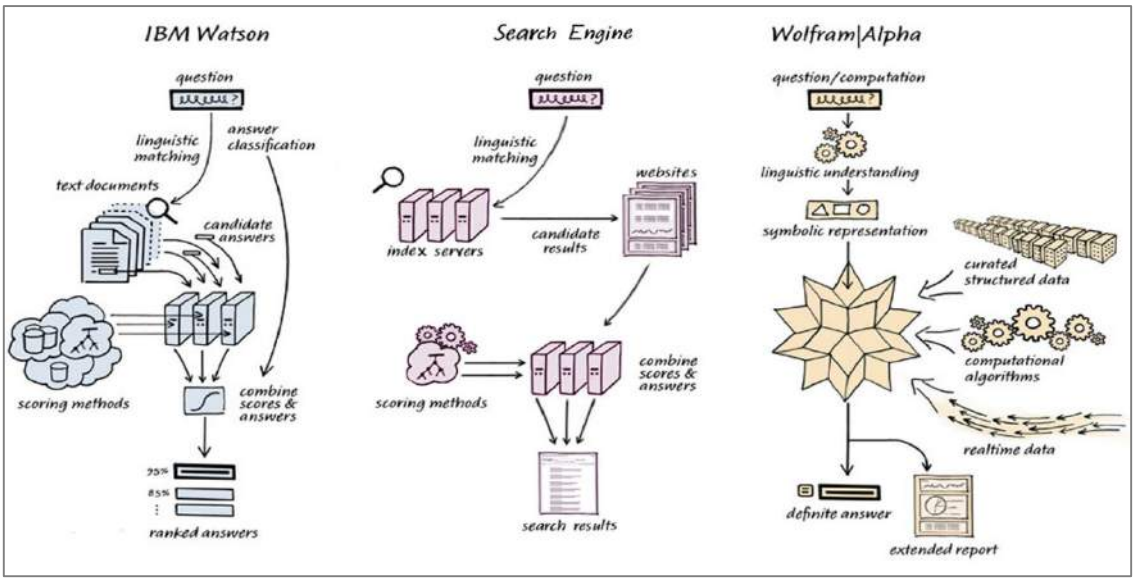


Fig. 102 – Comparison between IBM Watson's and Wolfram|Alpha's approach to answering a query, adapted from [486]

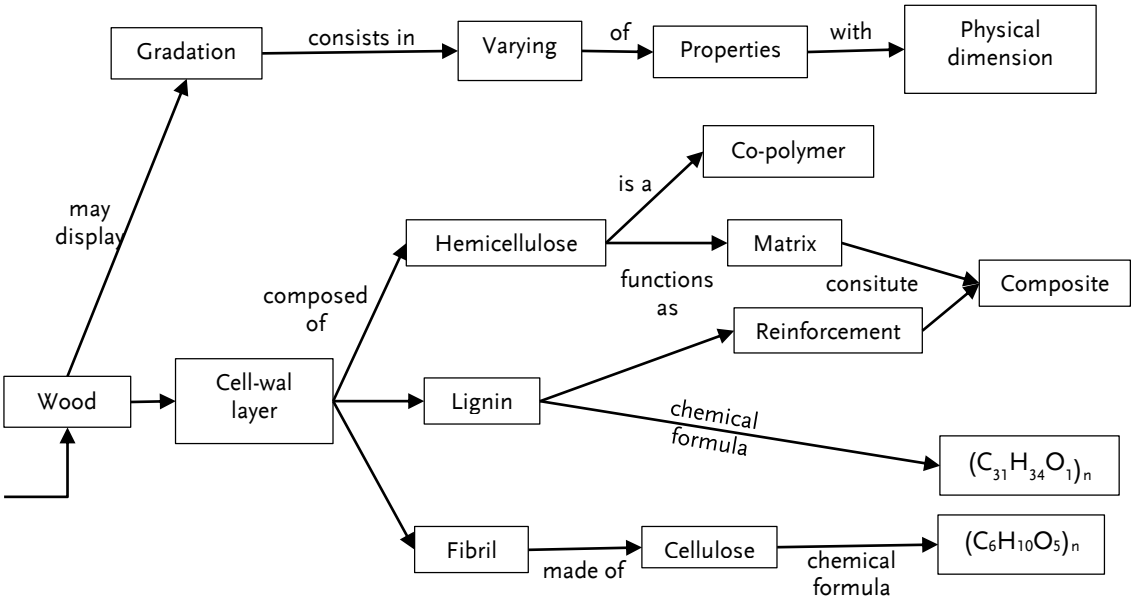


Fig. 103 – A simplified knowledge representation of wood composition for description logics.

For example if a biological mechanism is found that can be encoded to "composite material with high self-healing ability" it would then be stored in the database, and the computer would be able to use that information to the user when asked for self-healing composites. It would be faster than having to go through scientific papers to find such a healing mechanism which, many times, are in biological terms and thus an engineer looking for such a function to put in his material system would take longer to find it.

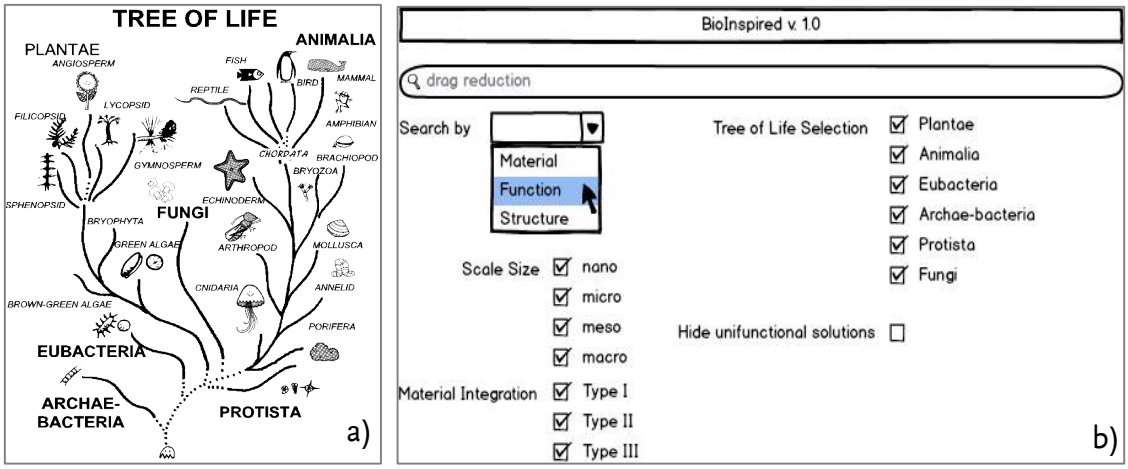
By using deductive and statistical reasoning it would make inferences that would lead it autonomously to conclusions such as

Wood has structures in the nanoscale.
Wood has structures in the microscale.
Material systems that have structures in several scales are multiscale.
Wood is a material system.
∴Wood is a multiscale material system.

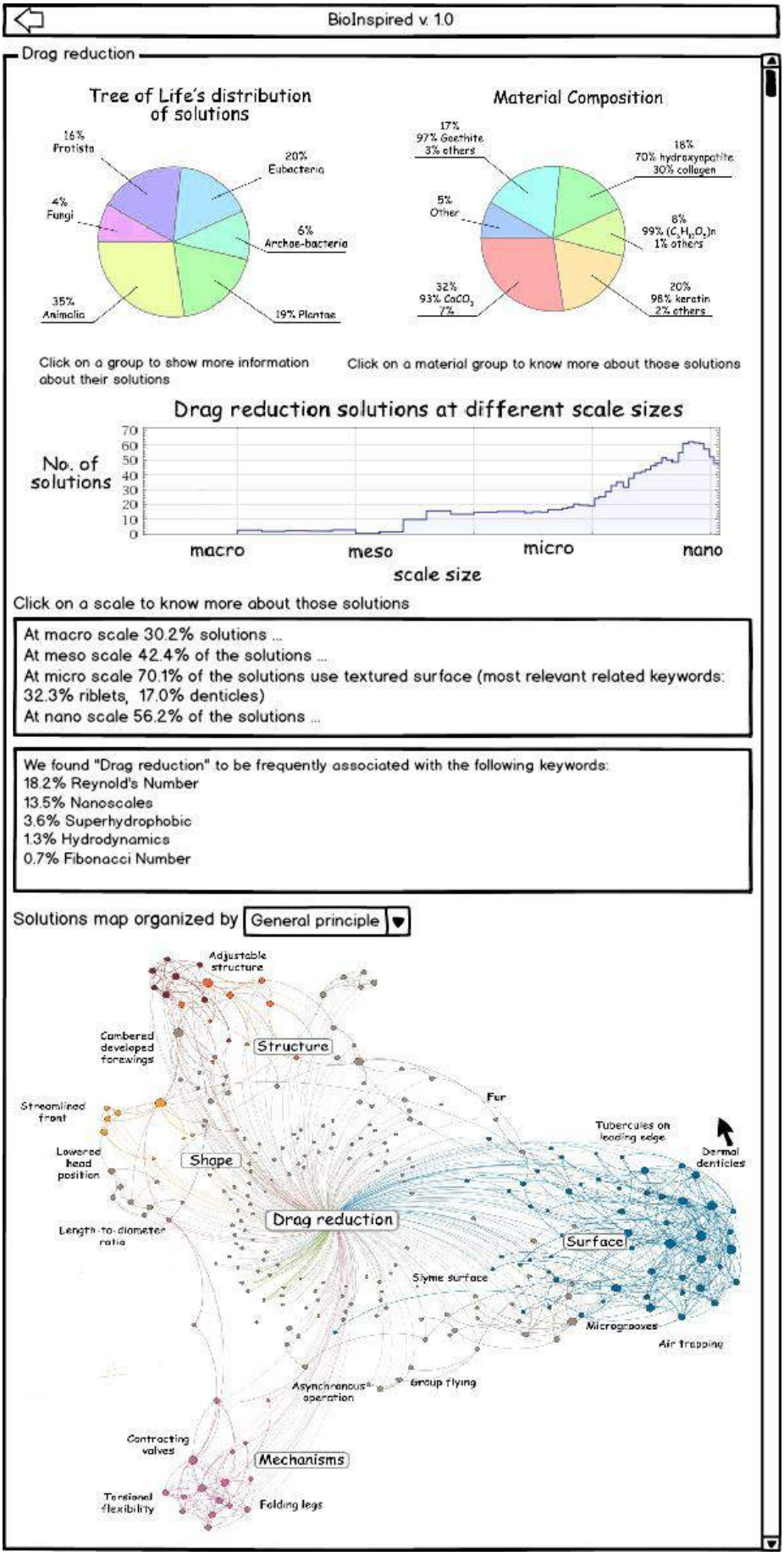
That is, self-learning. This would mean for example that wood would come up as a result if we wanted a multiscale material, even if no one had coded into the program that wood was such a material.

Later on image analysis could be implemented such as improved versions of Imagine Identify (https://www.imageidentify.com/), Merlin Bird Photo ID (http://merlin.allaboutbirds.org/photo-id) or Oxford's Semantic Image Segmentation (http://www.robots.ox.ac.uk/~szheng/crfasrnndemo). The former is a work-in-progress image identification web-based software that is able with a moderate rate of success to identify what is in a certain picture.

We can devise what would a software or web-based application for aiding in bio-inspired design could look like (**Fig. 104 b**). It would allow filtering by scale-size, material integration, life's kingdoms[4] (**Fig. 104 a**). It's knowledge would be ontological, alike Wolfram|Alpha. For a given material, function or structure it would then show higly organized information presented in a visual way. It would be able to semi or fully autonomously scan whatever the way studies are published at the time, be it papers, or entries in some online database, including the information presented in the images.



[4] Currently the most commonly accepted is the one proposed by Cavalier-Smith and subsequently revised [482]


BioInspired v. 1.0
Drag reduction
Tree of Life's distribution of solutions
16% Protista
20% Eubacteria
4% Fungi
6% Archae-bacteria
35% Animalia
19% Plantae
Material Composition
17% 97% Goethite 3% others
18% 70% hydroxynpatite 30% collagen
5% Other
8% 99% (C6H10O5)n 1% others
32% 93% CaCO3 7%
20% 98% keratin 2% others
Click on a group to show more information about their solutions
Click on a material group to know more about those solutions
Drag reduction solutions at different scale sizes
No. of solutions
70
60
50
40
30
20
10
0
macro
meso
micro
nano
scale size
Click on a scale to know more about those solutions
At macro scale 30.2% solutions ...
At meso scale 42.4% of the solutions ...
At micro scale 70.1% of the solutions use textured surface (most relevant related keywords: 32.3% riblets, 17.0% denticles)
At nano scale 56.2% of the solutions ...
We found "Drag reduction" to be frequently associated with the following keywords:
18.2% Reynold's Number
13.5% Nanoscales
3.6% Superhydrophobic
1.3% Hydrodynamics
0.7% Fibonacci Number
Solutions map organized by General principle
Adjustable structure
Cambered developed forewings
Structure
Streamlined front
Fur
Tubercules on leading edge
Dermal denticles
Lowered head position
Shape
Drag reduction
Length-to-diameter ratio
Surface
Slyme surface
Microgrooves
Air trapping
Asynchronous operation
Group flying
Contracting valves
Mechanisms
Torsional flexibility
Folding legs

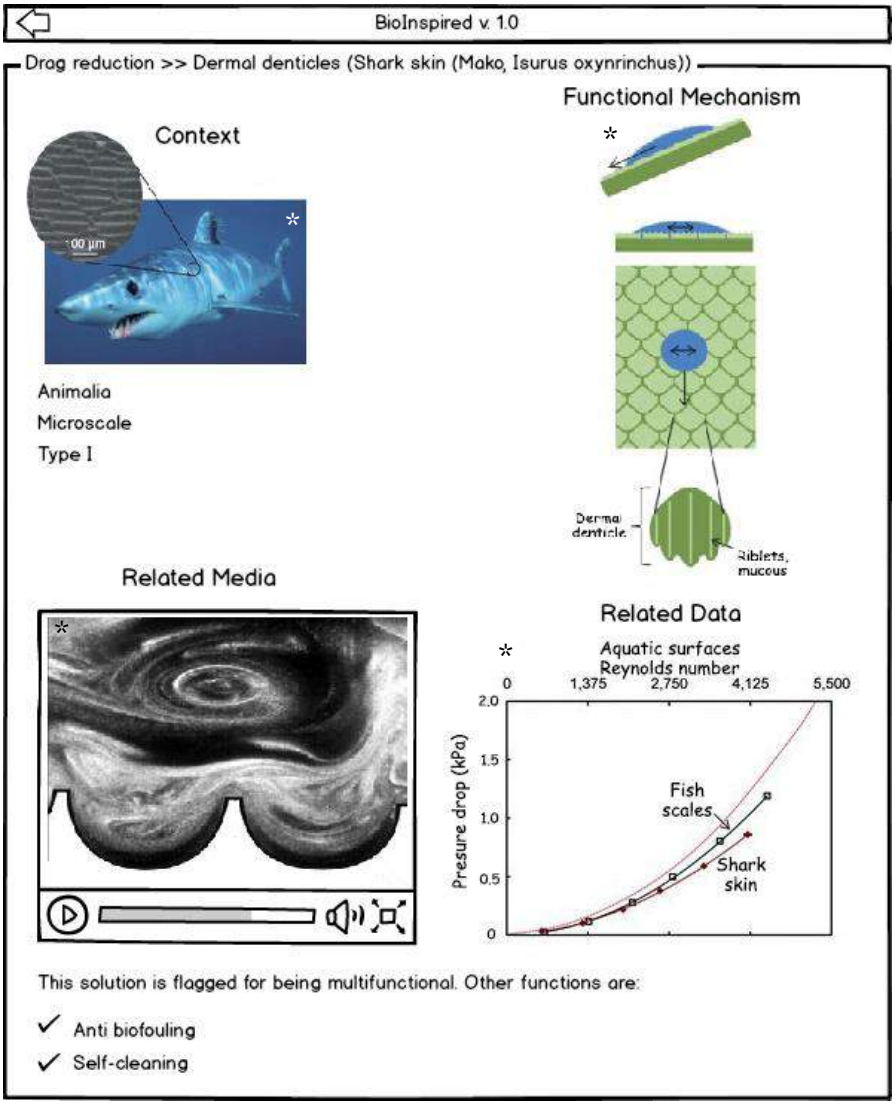


Fig. 104 – a) Life organization according to Cavalier-Smith [487]; b) Mockup of a possible biological solutions aggregator and analyzer for a web-based application. Images with '*' from [445]. Created with Balsamiq®.

A software/web-based application like this would immensely facilitate human creativity in devising new bio-inspired solution, and it would be the first step in streamlining the steps of acquiring and organizing information in the bio-inspiration process both for problem-driven and solution driven approaches.

4.3 Taking Advantage of Size Effects and Using Fractals

Fractals

Fractals might be a way to create easily programmable hierarchical, high surface area structures. The Koch Curve (also known as the Koch Snowflake) is a mathematical curve obtained by repeatedly replacing each segment of a generator shape with a smaller copy

of the generator (**Fig. 105 a**). In doing so the total length of the curve gets bigger, approaching infinity as long as we keep iterating. Fractals can also be created by repeatedly calculating simple equations whose results feed on the next calculation.

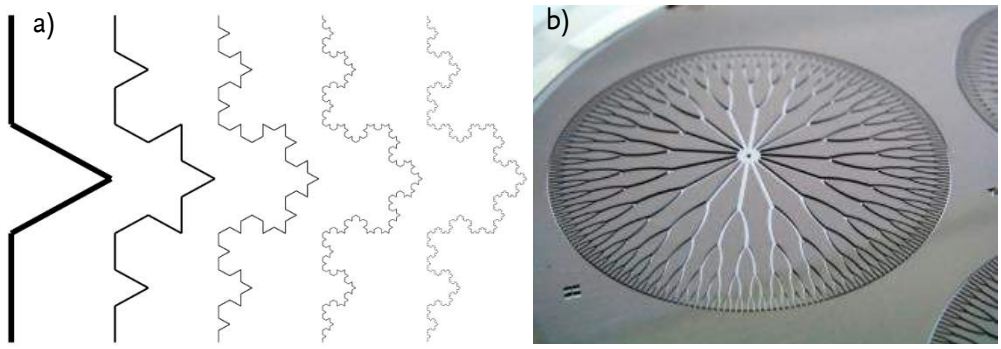


Fig. 105 – a) The Koch Curve; b) A cooling chip circuit designed in a fractal branching pattern by researchers at Oregon State University [488].

Manufacturing technology is the limiting factor because these patterns are easy to program. The fact that it is derived mathematically and consists of repeating patterns of equal shapes may allow for a better reproducibility and also could be very promising for applications where surface area is important such as adhesive, substance repellence and self-cooling/high heat-transfer rate (**Fig. 105 b**).

Size Effects

The size of clusters of atoms influence melting point, phase definition, mechanical strength, optical and thermal conductivity, heating capacity – which can even become negative, that is decreasing temperature with heating – , magnetic properties and catalyst behavior [489]. For example, nano-sized clusters of atoms of copper are transparent, platinum are catalysts, aluminum becomes a combustible material, gold turns liquid at room temperatures and silicon becomes a good conductor.

These properties are attributed to surface effects, flaw insensitivity and quantum size effects. The former is about how smaller clusters of atoms have a higher percentage of surface atoms than bigger clusters (the surface-to-volume ratio introduced in the chapter of carbon nano materials). And the surface atoms behave slightly different than those on the inside. The second is related to the fact that as the size of materials reduce, they become increasingly insensitive to cracks and defects, even existing a critical size below which full insensitivity is reached, and hence the strength of the material approaches its theoretical limit instead of being limited by the stress concentration around the flaws. This might be the reason why in nature many organisms and materials have their building blocks at the nanometer length scale at least in one dimension [490]. Finally, when material's size is reduced, the averaging of all the quantum forces that are responsible for the bulk material's properties no longer works, and the individual behavior of atoms and molecules takes precedence.

In practical terms, we can take advantage of these effects by producing materials that are nanoscale in one or more dimensions (**Fig. 106**) and using them for multi-scale composites or hierarchical structures.

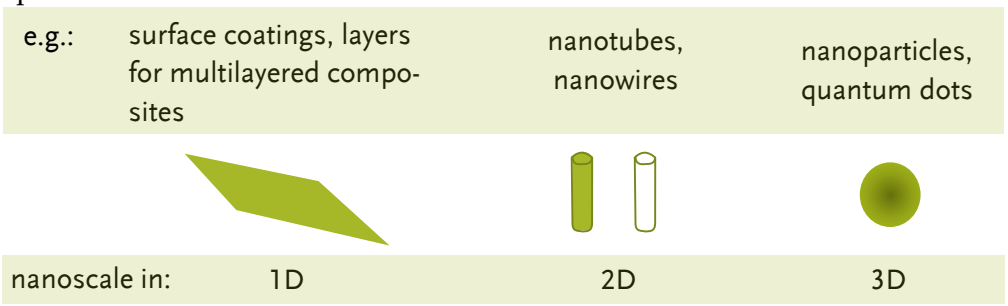


Fig. 106 – Examples of 1,2 and 3D nano-scale structures.

Earlier, a good example of this has already been shown where a nanolattice of a ceramic was found to be much tougher than expected (**Fig. 86**) due to a decreased number of flaws.

So far we've mainly focused on material system and products innovation, but it is also necessary to think about their performance and also the new place in the design process of these highly tailorable more complex MFMS that are being developed.

4.4 On Design, Optimization and Performance

Rethinking design procedures

Traditionally, parts are designed and then a material that meets the requirements of the application is selected on material databases based on its properties. This is a view shared by both engineering books and undergraduate project design courses [491, 492]. In the industry the materials scientist is often only required to characterize data or troubleshoot a problem after design.

However, as materials increase in complexity, tailorability, multifunctionality and number, the consideration about the material, now integrated with structures for greater multifunctionality, might need to be earlier (**Fig. 107**), at least in high performance applications, where the higher tailorability and resultant performance can more easily outweigh the increase in cost. For these cases, **multifunctionality, and therefore material design, should be present in the concept development or the system-level design phases.** For example, if a car hood is to have energy storing function and sensing abilities (to detect a hit for example) considerations about its weight and how exactly the sensing ability will integrate with the rest of the vehicle are made at the system-level design phase, which means the material system will enter the design process earlier than the usual detail design phase.

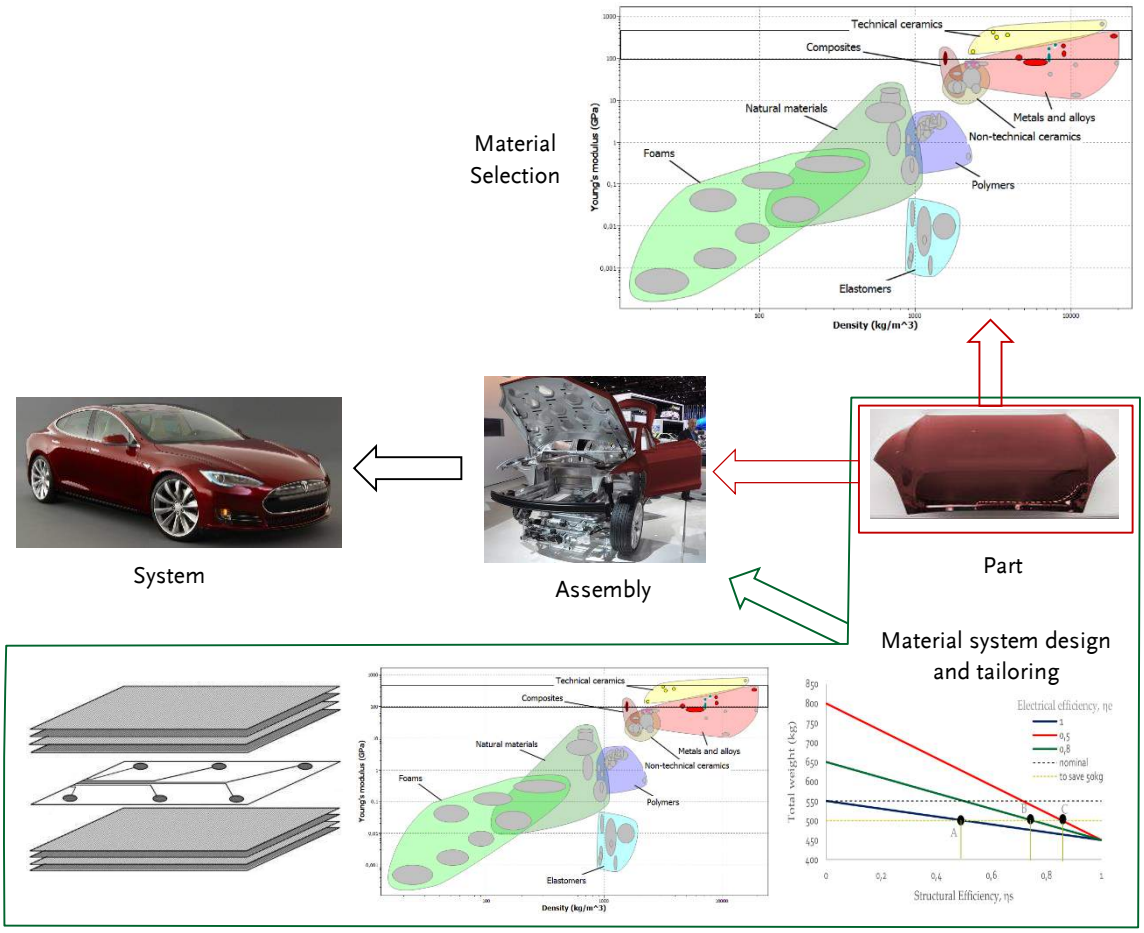


Fig. 107 – Simplified design process. Red: material is chosen and as an almost independent process from part design. Green: Part and material are designed concurrently as an integrated process. Images from [493, 494] and material selection graphics from Granta, CES Edupack 2014®, with adaptations.

In fact, as a guiding rule, we could say that generally **the more functions a material system has, the earlier it needs to be addressed in the product development process**.

If we take a typical product design process based on Ulrich and Eppinger's [371] we can represent on it the phases where the increase in functionalities performed by material systems should have the most impact (**Fig. 108**). Below is the reasoning behind each of the phases I believe will be the most impacted and the respective reasons.

In product specifications because the greater the number of functionalities performed by the material systems, the greater the number of metrics that depend on them. It is to be expected that future multifunctional materials will be normalized so that in many cases product developers still only need select materials instead of having to tailor them, especially for low demanding applications. Still, it will be possible to tailor the material system in ways that aren't currently possible. How much tailoring will be done depends on how close the normalized material system is to the targeted ideal values of the metrics it concerns. A trade-off analysis may be necessary, and that will require some new tools

for optimization and performance evaluation such as the ones mentioned in the following chapter.

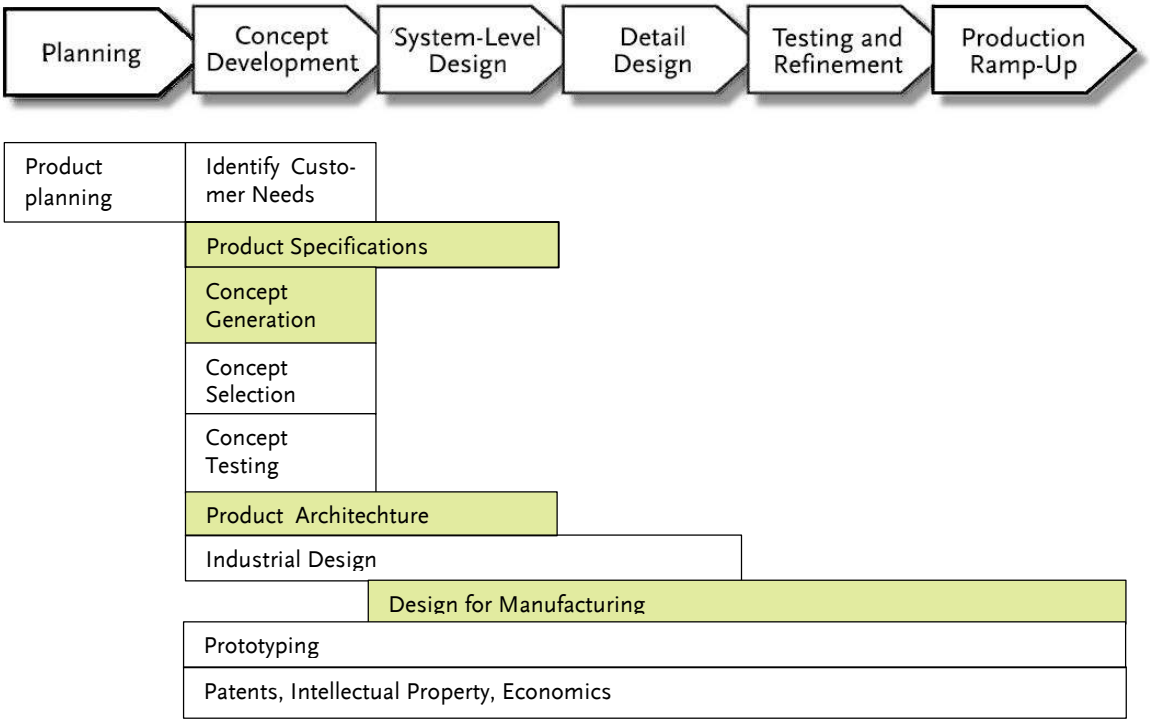


Fig. 108 – Product development process. In green, steps where new paradigm of material design should have the most impact. Adapted from [371, 495].

In the **concept generation** because the concept of a product is a rough description of the technology, working principles and the form of the product. The addition of MFMS can fundamentally changes all of those. For example, the description of a garment with human health monitoring capabilities is very different whether that is accomplished by the garment itself or a separated sensor system that happens to be bound to the garment.

In **product architecture** because of the concept modularity. A product has a very modular architecture when its functions are performed by separate components (modules) and integral architecture when the components are multifunctional. In other words, how easy it is to replace a module without impacting the rest of the system? In the case of MFMS, removing a function in many cases will result in the need to choose or redesign a completely different material system. For example if we were planning to use the power-fiber on a textile (**Fig. 57**) but then decided we don't need energy storage but rather energy harvesting, then the material system has to be completely redesigned/chosen. With this, it's easy to see that with the adoption of MFMS products will tend to have an integrated architecture, and therefore they will also impact this phase.

Finally, in **design for manufacturing**. The economic success of a product is highly dependent on the manufacturing cost. A product can have billions of sales but an economic failure because it failed to generate profit. This can be because the cost of manufacturing

was too high. A design that promotes economic design is able to keep high quality while reducing manufacturing cost. As we saw before, manufacturing is one of the challenges that so many of the new MFMS face. Also if the field of manufacturing is already one of the most integrative in terms of different departments having to work together, then it is about to become even more, as one of the main facets of multifunctionality is precisely multidisciplinarity. As functions from different fields become highly integrated, it becomes slightly harder to discuss manufacturing issues if for example the person responsible for the biological systems from which the product or part of it was inspired is missing in the discussion, because each function has a higher dependency on the others.

Optimization and Performance

In terms of optimizing the material systems themselves, Sigmund et al. [496, 497] have developed topological optimization methods for type III material systems with very different physical mechanisms to determine the optimal performance, having simulated many functional combinations with up to 3 material phases. Their theoretical work has been validated by the similarity between their solutions and ones found in biological systems.

For type I and II material systems, Thomas and Qidwai have developed too some optimization tools namely the introduction of the concept of materials architecture [245, 498] in order to allow the use of the materials index, as developed by Ashby et al. to rank the performance of materials with regarding system-related objectives such as mass, cost or density [499, 500].

Qidwai et al. proposed a few guiding rules [245] concerning the addition of multifunctionality to systems which served as inspiration for the following guidelines:

Start by trying to add new functionality(ies) to the material with a more complex function. E.g. If in a specific case the complexity of energy storage process is greater than that of elastic deformation, it might be easier to add structural function to the energy storage system rather than add energy storage capabilities to the structural system.

Target unifunctional mid to low performance parts. For example, there may be more performance gains to be realized by adding a new function to structural parts subject to lower and not critical structural loads. A good example of this is the aileron in the previously mentioned Lola-Drayson Racing EV [248].

Adding multifunctionality must have as its primary goal the increase of system-level performance, even if the subsystems' individual performance is decreased. In adding electrically conductive fillers to a composite to make it electrically conductive, one might have a lower electrical performance than if simply added electrical wires. In order to create a structural battery, one might have to reduce its energy density. However for the system as a whole, the energy density might be greater due to the inexistence of unifunctional structural materials.

Let's have an example of trade-off considerations in a structural battery for a simple aircraft such as the airbus e-fan (**Fig. 109**). Methodology from [34].

The main objective is that even though we may lose efficiency on each of the subsystems we improve overall efficiency. So we may end up with a system with less capacity and less bearing capability, but the net weight loss surpasses those effects. As we saw in the beginning of chapter 2, a decrease in the weight of the aircraft increases by 1.5 times the flight time whereas an increase in battery capacity only increases the same variable by a factor of 1. So it is useful to combine both in order to save weight.

550kg (total plane's weight) = ~100kg (battery) + ~450kg (structure), with

η_s = structural efficiency, $0 < \eta_s < 1$
η_e= energy storage efficiency, $0 < \eta_e < 1$

If we were to make the plane using a structural battery resulting in $\eta_s = 0.74$ and η_e = 0.8 (point **B**, in **Fig. 110**), it would mean the materials would be able to bear 74% of the loads the nominal composite can and store 80% of the energy the battery stores. So that's a 20% decrease in flight endurance time from the loss of battery efficiency.

Recording from an earlier chapter that a reduction in weight increases flight endurance 1.5x more than an increase in battery capacity. Which means that for a solution to increase flight endurance time the following inequation must be valid

$$1.5 \cdot \frac{mass\ savings}{nominal\ mass} > (1 - \eta_e)$$

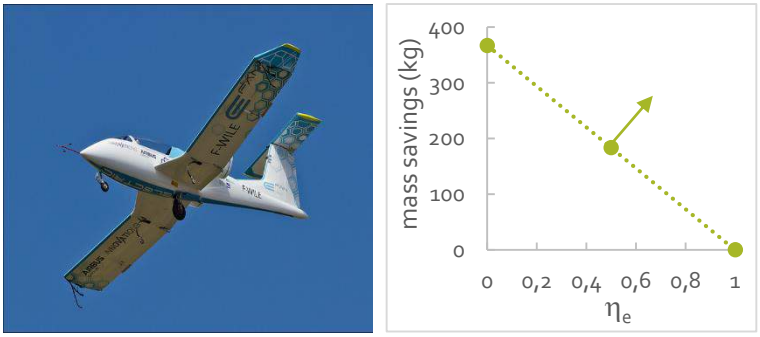


Fig. 109 – a) Airbus E-Fan: a prototype two-seater electric aircraft being developed by Airbus Group first demonstrated at an airshow in UK in July 2014 [501]; b) Plot of the inequation above. Mass savings must be greater than the dotted line for a given energetic efficiency.

So if we had reached the conclusion that adding structural function to a battery would be easier, and hypothetically we knew that a structural battery has $\eta_e = 80\%$, then mass savings need to be greater than 73.3kg for the flight endurance time to increase (Point **B**), which also means that $\eta_s \geq 0.74$. This results in a very small domain (orange in **Fig. 110**) of possible values. Point C would be unacceptable because we would need greater mass savings to compensate for a 50% loss in energy capacity from the battery.

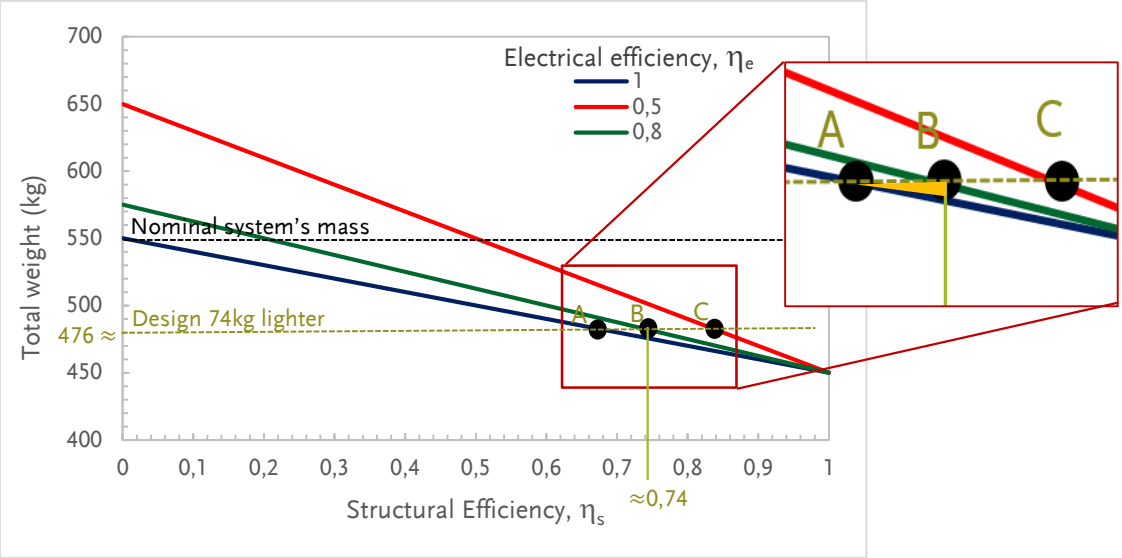


Fig. 110 – Design considering that η_e=0,8. Inset represents acceptable domain of values in orange.

It is possible that the combination of two functions increases the performance of both. The abalone shell is a biocomposite that is 98% m/m calcium carbonate (Aragonite or $CaCO_3$) and 2% m/m protein. However, it is 3000 times tougher than either when considered alone or their mixture according to the rule of mixtures. Similar situations can be observed for bone and alumina/PMMA composite (**Fig. 111 a**). This is because of complementary intrinsic and extrinsic contributions throughout their hierarchical structure (**Fig. 111 c**)[382].

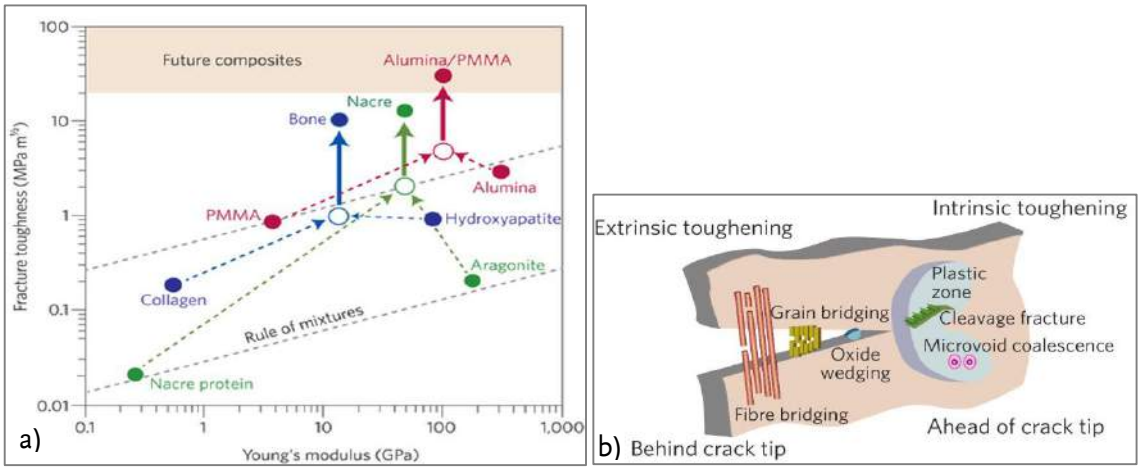


Fig. 111 – a) Bone, Nacre and Alumina/PMMA composite as materials whose toughness is far greater than that of the materials that constitute it. Closed and open circle represent crack growth and initiation respectively; b) Extrinsic and intrinsic toughening mechanisms present in bone, which are responsible for its far greater crack growth propagation than what the rule of mixtures would predict [382].

It is easy to imagine a situation where something similar would happen for the example of the airplane. In a composite where the fiber bridging is done by some form of electro active fibers that increase their strength when current passes through them. In that situation adding a battery to the structure would result in $\eta_s > 1$.

Only the surface of this topic has been scratched, because there is a lot of potential for performance evaluations techniques, but the basis were presented. Now, other very important aspects that all of these design and performance evaluations need to take into consideration before a final decision is made, are going to be presented.

4.5 Increasing Sustainability and Environmental-friendliness

Growing New Materials

Biology is great at solving complex problems, in very harsh environments, where failure means the eradication of that particular gene. Even though our current production methods are limited in the way that we can't for example create intricate hierarchical nanoarchitectured multimaterial systems, nature has been producing them for billions of years. So why not try some of nature's mechanisms for creating these structures and materials and widening their pallet of elements that they can use from carbon, hydrogen, oxygen and a few others, to the whole periodic table? Or changing the architecture of the nanomaterials/structures to our fitting? Fortunately this is something that has captivated the attention of some. Below, four examples are presented.

Fungi, along with bacteria, are nature's best recycling systems, where the mycelium, their vegetative part, is where material transformation occurs. For example, in order to replace Styrofoam, Bayer et al. [501] developed a bio-degradable foam which is self-assembled by mycelium and biomass and can be transformed into almost any shape having good fire and humidity resistance and thermal, electrical and acoustic isolation properties.

Krogstad presented his PhD thesis in 2012 on aqueous self-assembled materials [502]. He was able to synthesize some materials but with some difficulties in predicting the resultant structure.

Bawazer et al. [503] manufactured a semiconductor material synthesized by enzymes that were put through a processes of "directed evolution" similar to selective crop and animal breeding where one only allows the crops/animals with certain genes/phenotypes to breed so that next generations all have them. In this case they used silicatein, which is the same enzymatic protein responsible for the formation of silica skeletons in marine sponges. At the end of the reproductive process they would have a large gene pool manifesting itself with silicateins of different properties. Then they chose the silicateins that had the properties they wanted, in this case, that exhibited a mineralization process.

Belcher's et al. [504] took a similar approach by engineering viruses, through directed evolution, whose coating is able to bond with lithium. By packing together millions of

lithium-ion coated viruses they were able to create positive and negative electrodes, being able to produce an actual battery. That is, a battery made out of viruses. This same technology was also used for the production of improved solar panels [505].

So basically from this works is convincing simple organisms to work with a new toolbox, for example with the rest of the periodic table, in order for them to produce a material/structure that we want. The convincing part would be through coding the DNA sequence that tells them to do it, and inserting it into the organisms. The organisms would then build something new out of resources they would not normally have used.

Using Natural Organic and Inorganic Materials in Different Ways

Instead of having to produce materials through complicated manufacturing processes that involve high energy costs, wastes, and the need for several chemical products to be used, what better than to obtain them from waste products from other industries or from nature's raw materials requiring simple treatments? This is the idea behind a class of materials with the bio- prefix: bio- -materials, -plastics, -polymers, -based nanocomposites, -nanocomposites, and so on.

In the next paragraphs a quick overview and a few examples for two promising biomaterials are presented.

Cellulose

Cellulosic composites with cellulosic nanofibers as the reinforcing phase are currently regarded as one of the most promising research areas in the field of plant products. A cellulose fiber is basically composed by a bundle of microfibrils, which are composed by long chains of glucose molecules (**Fig. 112**). The reasons that make this natural material so attractive are:

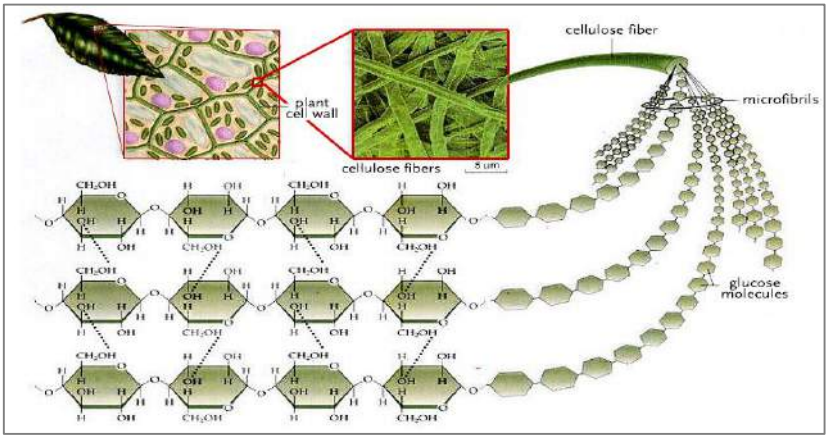


Fig. 112 – Structure and composition of cellulose in a leaf. Adapted from[506].

1) It's the most common organic polymer and can be considered close to an inexhaustible source of raw material for eco-friendly materials and products [507];
2) It's reported high stiffness (100 < E < 160 GPa) [508]) ;

3) High aspect ratio of cellulosic fibers (L/d) makes them good candidates for a reinforcing material as this facilitates stress transfer from the matrix to the reinforcing phase [507];
4) It's low weight, biodegradability, and renewability [509].

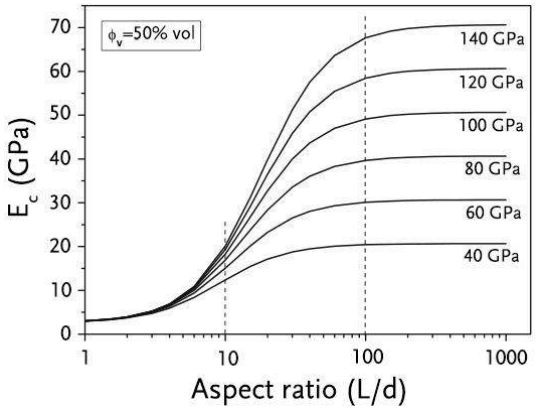


Fig. 113 – Plots for the Halpin–Tsai equation for fibers with a range of Young's Moduli of 40–140 and the respective predicted composite modulus (E_c) depending on the fibers' aspect ratio. Adapted from [508].

Compared to natural fibers like flax and hemp (E=40-60GPa), and single cells (E<80GPa), cellulose nanofibrils and nanowhiskers have a higher Young's modulus which, combined with their high aspect ratio brings major mechanical benefits for the composite compared to micro-sized fillers (**Fig. 113**).

Wood is currently the most important source of cellulosic fiber, however we would clash with the paper and construction industry and besides, creating another reason to cut down trees is not sustainably intelligent. For this reason, cellulose for incorporation in novel materials should be coming either from waste products of those industries or from by-products from crops, which is exactly what some companies are doing.

AgriPlas (from wheat straw) – For example a company named A. Schulman Inc. [510] has been producing and selling a plastic they named AgriPlas, already used in consumer goods such as some components on the Flex Ford automobile [511]. This plastic has incorporated wheat fibers derived from wheat straw, which is generally treated as a waste product from wheat grains. It resulted in a lighter, with a lower CO_2 footprint and lower dependency on petroleum composite plastic.

Biomid (from cellulosic waste) – Biomid, as another example, is a 100 percent cellulose-based fiber with a fiber density of approximately 1440kg/m^3, specific modulus very close to E-glass, and with a specific tensile strength comparable to Innegra Technologies' (Greenville, S.C.) 8g/denier high-modulus polypropylene (HMPP) fiber [512].

The most interesting aspect though is that the fiber's raw material comes from wood pulp and paper-industry waste. For this reason the producer, Shark Consulting, claims it has a smaller carbon footprint even than other natural fibers. As a matter of fact, they

claim its manufacturing generates only 0.88 kg of carbon dioxide (CO_2) emissions per 1ton of fiber, compared to 55 kg for flax fiber and 500 to 600 kg for glass fiber.

Cellucomp (from root vegetables) – Cellucomp, a Scottish material company founded by material scientists uses wastes from root vegetables, currently using mainly beet pulp, from which they extract cellulose.

Current applications for cellulose nanofibers are adhesive reinforcement, optically transparent paper for electronic displays, in DNA-hybrid materials, for use in hierarchical composites for foams among others. Current reviews on state of the art and applications have been recently done [507-509].

Some very recent interesting developments, not present on those reviews are how it has been showed that it is possible to 3D-print cellulose based materials and to make a light emitting flexible transparent nanocellulose paper. Concerning the former, the researchers did it by mixing cellulose nano fibrils with a hydrogel, which is made of 95-99% water, it was possible to run the mix in the 3D printer, and then by adding in CNTs the researchers were able to achieve electrical conductivity [513]. Concerning the latter, they dispersed ZnSe quantum dots in a nanocellulose paper

Both developments are very interesting because they allow a greater infiltration of this natural material in the market by finding more uses for it, especially in fields traditionally dominated by artificial materials.

Some challenges remain, namely, obtaining a uniform distribution of the fibers in composites' matrices [508] and the separation of plant fibers into their smaller constituents for the extraction of cellulose [509].

Yes, cellulose is both ubiquitous, environmentally friendly and overall promising. But it's not the only one.

Basalt fibers

Basalt is a volcanic rock and the most common one on Earth's crust (1/3 m/m). It is composed of the most common materials: SiO_2 (49.97% m/m), Al_2O_3 (15.99%), CaO (9.62%), FeO (7.24%), MgO (6.84%), among others. These rocks have been used to produce basalt fibers from a similar manufacturing process as glass fiber, though simpler – with lower temperatures and less additives. The price of basalt fibers lies in-between S-glass and E-glass fibers though it can vary depending on their quality. Their relatively high mechanical properties (**Table 10**), higher oxidation resistance, higher radiation resistance, higher compression strength, and higher shear strength than carbon and aramid fibers are some of benefits of using these fibers [514, 515].

Table 10 – Typical values of basalt fibers [515].

ρ(kg/m³)	E (GPa)	Tensile strength (MPa)	Strain at break (%)	Service temperatures (°C)
2700	89	4840	3.15	-269 - 650

Unlike graphene and CNTs, sometimes a material is not obviously good from the start. Even though the future of these fibers is yet to be seen, they have been researched since the 1920's, so it took a long time and several waves of interest and disinterest, before the more recent promising advances [514, 516].

Energy Harvesting Possibilities

In trying to improve electric devices' independence there are 4 main areas of focus:

1. to improve the energy density of the energy storage systems (batteries or capacitors);
2. to reduce power consumption ;
3. to develop self-powered devices which generate or harvest energy or
4. to transmit the power from a centralized power source.

Currently for MFMS the third area is the one that has received the most attention. *Energy harvesting* or *power scavenging* are expressions that mean *to extract energy from the environment*. The goal in this research field has been to either generate low-power electricity (<1W) or to recover energy from wasted or unused power. This would enable self-powered electronic devices to work for years without needing any external recharging.

More, since the energy from sources that emit them are in their majority renewable and mostly resultant from energy waste (**Table 11)**, harvesting it has a direct beneficial effect on sustainability, the environment and health.

The applications for this technology range from electronic wearable devices to wireless applications such as remote wireless sensor networks that are hard to access and are required to function over extended periods of time used in structural health monitoring.

Table 11 – Sources of energy available in the surrounding which are/can be tapped for generating electricity [517].

Human Body	Vehicles	Structures	Industrial	Environment
Breathing, blood pressure, body heat, walking, arm motion, finger motion, jogging, swimming, eating, talking-	Aircraft, UAV, helicopter, automobiles, trains, tires, tracks, peddles, brakes, shock, absorbers, turbines-	Bridges, roads, tunnels, farm house structures, control-switch, HVAC systems, ducts, cleaners.	Motors, compressors, chillers, pumps, fans, conveyors, cutting, dicing, vibrating machinery.	Wind, solar, temperature gradient, daily temperature, ocean currents, acoustic waves, EM waves, RF signal.

When designing energy harvesting products or parts with MFMS there are some considerations to have in mind:

1) Relationship between power needed and power harvested:

a. $\dot{W}_{needed} > \dot{W}_{harvested}$ => needs energy storage, duty cycle of the system has to be low enough so that there's time to store sufficient energy while the system is on standby or sleeping for each time the system is on or active;
b. $\dot{W}_{harvested} \leq \dot{W}_{needed}$ => doesn't need energy storage if energy can be harvested at any time constantly;

2) Controllability and predictability of the energy sources [518]:
   a. **Fully controllable:** Energy can be generated and controlled as desired, e.g. user generating energy for a flashlight by shaking it;
   b. **Partially controllable:** Unpredictable environmental conditions may change the capacity for energy generation. For example harvesting the energy from another system. Even though that system can be controlled, since its main purpose is not to provide energy it may be unpractical to active it for that sole purpose;
   c. **Uncontrollable but predictable:** Harvesting energy from the sun is an example. The energy source can't be controlled yet the daily and seasonal cycles are known;
   d. **Uncontrollable and unpredictable:** The energy source cannot be controlled to generate energy when wanted and it is hard to predict when it will. Such examples are earthquakes, lightning strikes and outdoor vibrations due to e.g. passing vehicles.

There are 4 main ambient power sources to be considered, and the range of power available is represented in **Fig. 114**.

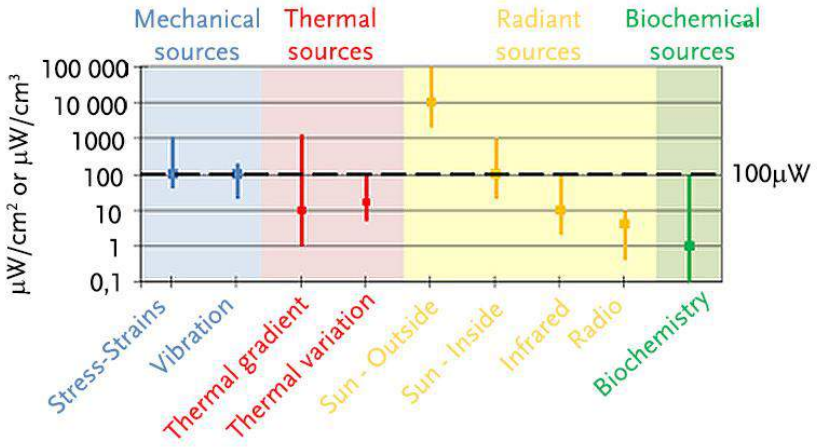


Fig. 114 – Main ambient power sources before conversion, adapted from [519].

In **Table 12** reviews and interesting papers about this topic are referenced.

Table 12 – Recent reviews or extraordinary papers on mechanical, thermal, radiant and biochemical power sources.

	Material system	**Sources** (mechanism)
Mechanical	Piezoelectric	[114, 168, 184, 193, 520-522]
Thermal	Thermoelectric	[523-526]
Radiant	Carbon nanomaterials, metallic nanostructures	[69, 93, 292, 527] (solar)
Biochemical	Biofuel cells	[528-531]
Other	Graphene	[70] (coupling of ions with free charge carriers)
	Paper, bacteria	[532]
	HYDRA	[533](evaporation energy scav-enging)

Next a very quick synthesis of each of the main energy sources is presented.

Mechanical

Vibrations and stress-strain are currently the type of mechanical energy that is the most scavenged. The piezoelectric effect and electromagnetic or electrostatic mechanisms can be used to convert kinetic energy being that the former, highly suitable for MFSM as we saw, have emerged as one prime methods for energy conversion from mechanical sources to electrical energy. This is the most historically successful way of energy scavenging, though the other sources are now catching up due to technological advances.

Thermal

The Carnot cycle provides the theoretical limit to energy obtained from a temperature difference. The Carnot efficiency is $\eta_C = \frac{T_H - T_L}{T_H} = \frac{\Delta T}{T_H}$, where T_L and T_H are the temperatures of the low and high temperatures sources across which the thermal generator operates. For small ΔT, Carnot efficiencies are very limited – for example, going from body temperature (37℃) to a cool room (20℃) only results in $\eta_C = 5.5$ %.

Still, even low values of efficiency, and corresponding low values of power, might be enough for very low power applications such as nanodevices to be used inside the human body, or reusing the heating by Joule effect of power lines (about 8-15% of the total energy generated at the power plant [525]) or the wasted heat from oil engines and electronic devices.

Radiant

Ambient radiation can be found ubiquitously especially in urban environments, however, barring the sun, the amount of energy is also suitable only for low-power systems.

Sources include:

- Mobile-phone towers and mobile phones;
- Wi-Fi transmitters;

- IR from hot engines and devices;
- Satellite transmissions;
- Sun;

Solar energy has by far the highest radiant incidence of all the sources, as we can see in **Fig. 114**. The power that can be harvested this way ranges from about 100mW/cm² if directed at the sun in a bright day and 100μW/cm² in an illuminated office (sometimes an algorithm can be used for extracting the maximum amount of power that a photovoltaic cell can produce called Maximum Power Point Tracking [534]).

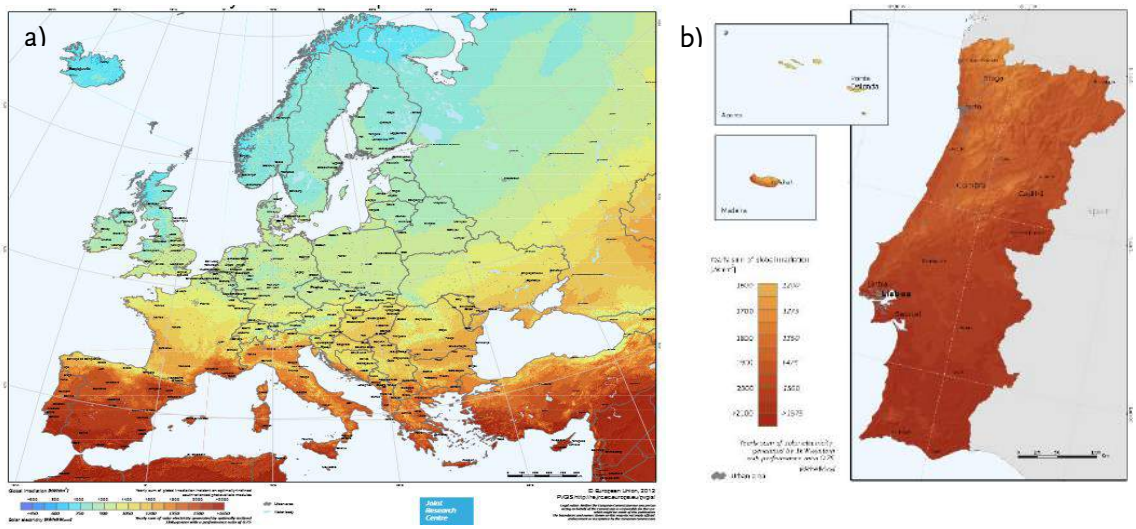


Fig. 115 – a) Photovoltaic solar electricity potential in European countries; b) Portuguese global irradiation and solar electricity potential at optimum angle [535–537].

A recent study from MIT showed that solar energy holds the highest potential for meeting the long term of humanity's energy needs in a sustainable way [538]. Portugal has the highest average incident irradiation per square meter of land from Europe (**Fig. 115**) which for us emphasizes even more the importance of developing solar harvesting material systems.

Biochemical

Recently the healthcare industry is experiencing a surge in interest towards wearable medical devices which can have the ability to monitor vital body parameters. Further progress has been hindered due to the lack of successful options for energy harvesting to power those devices [529].

This source of energy is the least related to sustainability but is nevertheless very interesting and useful, so I decided to include it here. This field is somewhat a challenge to penetrate linguistically for someone trained in mechanical engineering, so there might be more, but the main source of this type of energy seems to be biofuel cells, that is, an electrochemical energy scavenger that uses biological enzymes to catalyze reactions from energy packed biological reactants such as glucose to harvest electrical energy (sources in **Table 12**).

Other

Finally, there might be other untapped and under-researched energy sources. An example is evaporation. Recently Chen et al. created a set of exemplificative machines driven by a biologically inspired hygroscopy-driven artificial muscle (HYDRA) that are solely powered by changes in humidity due to evaporation [533].

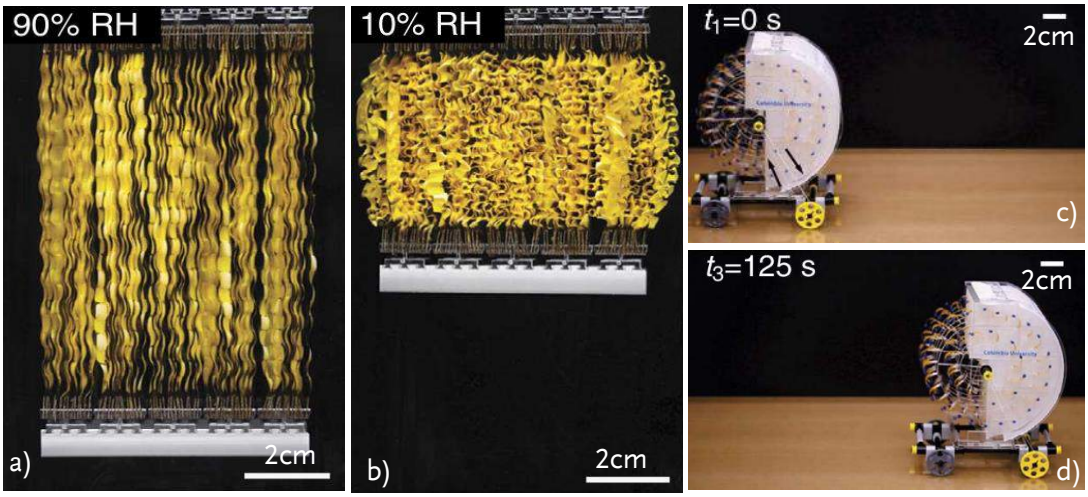


Fig. 116 – a–b) Hygroscopy–driven artificial muscles lifting their own weight at 90% and 10% relative humidity; c–d) Snapshots of a miniature actuated by the same material configured in a rotary engine [533].

With this, almost all of the main points of the chapter have been made, and the following two subchapters present a synthesis, consolidation and clarification of the major topics presented so far in this chapter.

4.6 The Process from Goals and Ideation to Adoption

In **Fig. 117** it is presented the general process both for MFMS innovation and product innovation containing MFMS.

The former, represented in yellow, mostly comprises work in discovering or improving material systems (e.g. graphene, better SMMs and *MFC*), phenomena (e.g. how light diffraction results in different colors) including biological (limpet teeth, drag reduction from shark denticles), and manufacturing methods (e.g. scalable CVD), which then may or may not be used to be integrated in or to produce MFMS depending on their interaction with other materials and manufacturing methods.

The latter, represented in brow, encompasses mostly the developing of products with concurrent material design, if needed, while assessing the efficacy of replacing unifunctional MS by MFMS.

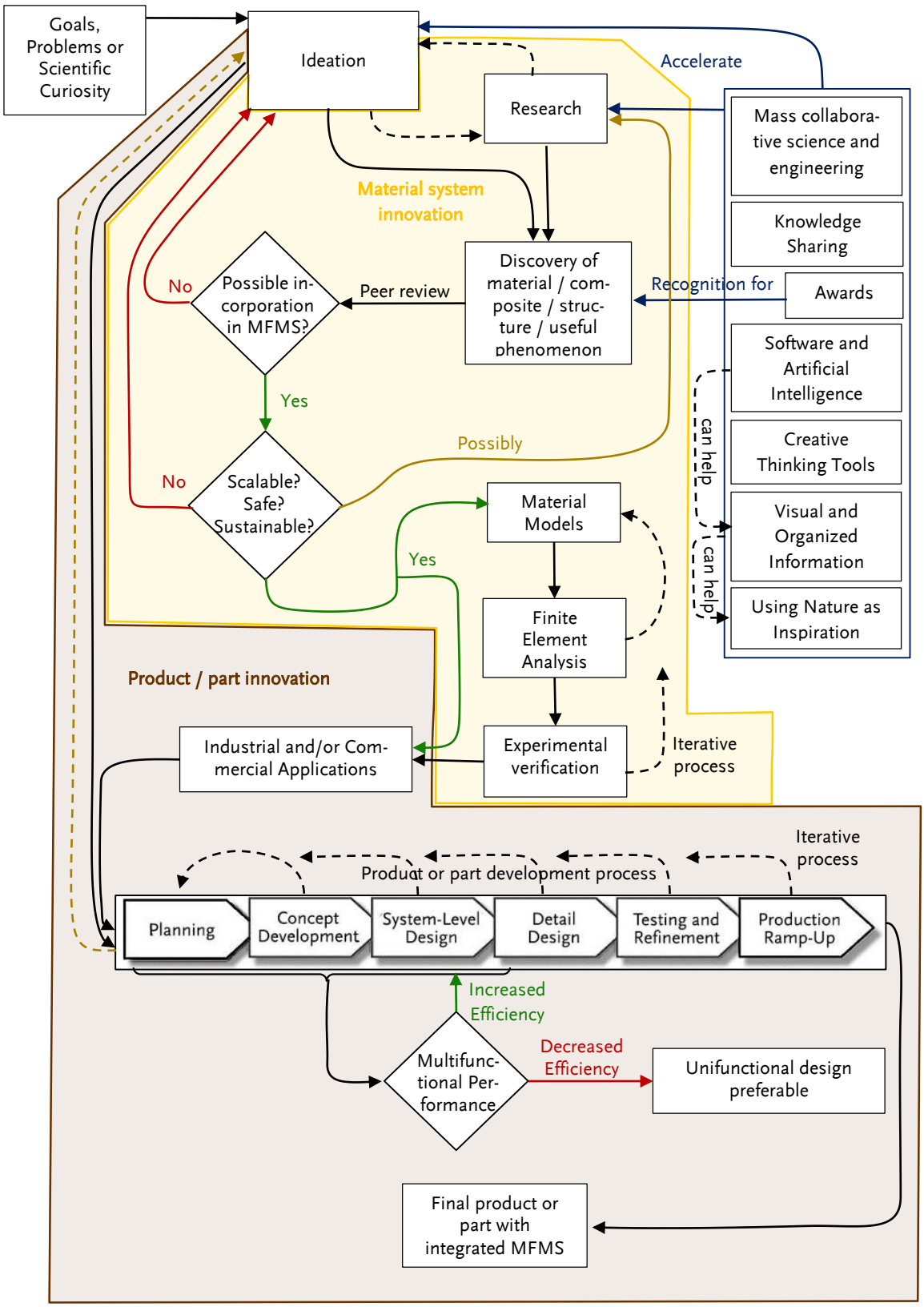


Fig. 117 – The process concerning MFMS and product / part innovation from goals to adoption of the existing or designed MFMS. Green, red, yellow arrows represent: positive, negative and neuter answer. Dashed lines represent optional paths.

4.7 Example of the Initial Stages in Designing a Simple Multifunctional Heart Abnormality Detector Instrument

Because examples are a great way to cement information, here an example that encompasses the topics (ideation, inspiration from nature, design process and multifunctional performance and sustainability) covered in this chapter is presented. For that reason, contrary to what would happen in a corporative setting, a broad goal and few constraints will be set. For example, customer needs, product specifications, time and budget planning will be skipped. The guideline won't be depth but breadth so as to cover the mentioned topics.

In Europe, cardiovascular diseases are the **main** cause of death for humans accounting for over 47% of all deaths in 2012 [539]. This will be the underlying motivation for the topic of this example. The goal for the product will be to detect and classify heart abnormalities by using a simple portable instrument, to be named HealthyHeart. Currently the detections of heart failure can be done in several ways. This list presents the most common (in bold) and current ways in which they are performed [540, 541]:

1) **Sound analysis**: heart and lung sounds;
2) **Visual:** swelling in body parts and appearance of certain veins, echocardiography, doppler ultrasound, magnetic resonance imaging, X-ray;
3) **Electrical:** Electrocardiogram, Holter monitoring, stress test;
4) **Chemical:** blood test;
5) **Various:** cardiac catheterization.

For the purposes of this example, let's simplify and focus on the analysis that right from the start appear to be simpler to perform: electrical and sound-based.

It is known that the electrical signal (voltage) and sound waves from the heart are sufficient for a myriad of diagnostics [542-544]. Mangione et al. [545] have reported how physicians in training and medical students identified cardiac events with their auscultatory skills, concluding that they correctly identified only 20%, value that didn't improve with further time in medical practice. Ideally the sonorous information would be analyzed by an AI[546] or a simpler software [547, 548].

Then the question arises on how to effectively measure or transmit sound waves and the electrical signals from the heart so that they can be correctly analyzed.

By **reasoning from first principles** we would study how the heart muscles are stimulated electrically to contract by electric impulses resulting from ionic concentration changes that spread through the myocardium (heart muscle) (**Fig. 118 a**). As that happens the electrical field produced in the myocardium continually changes in size and direction. In **challenging the status quo** we could first observe that in the most common 10 electrode, 12 lead electrocardiogram (ECG), a kind of 3D mapping of the electrical

activity of the myocardium is created. Ten electrodes are positioned so that a frontal view and a cross sectional top view (**Fig. 118 b**) are written in the grid paper by the electrocardiograph (**Fig. 118 c**).

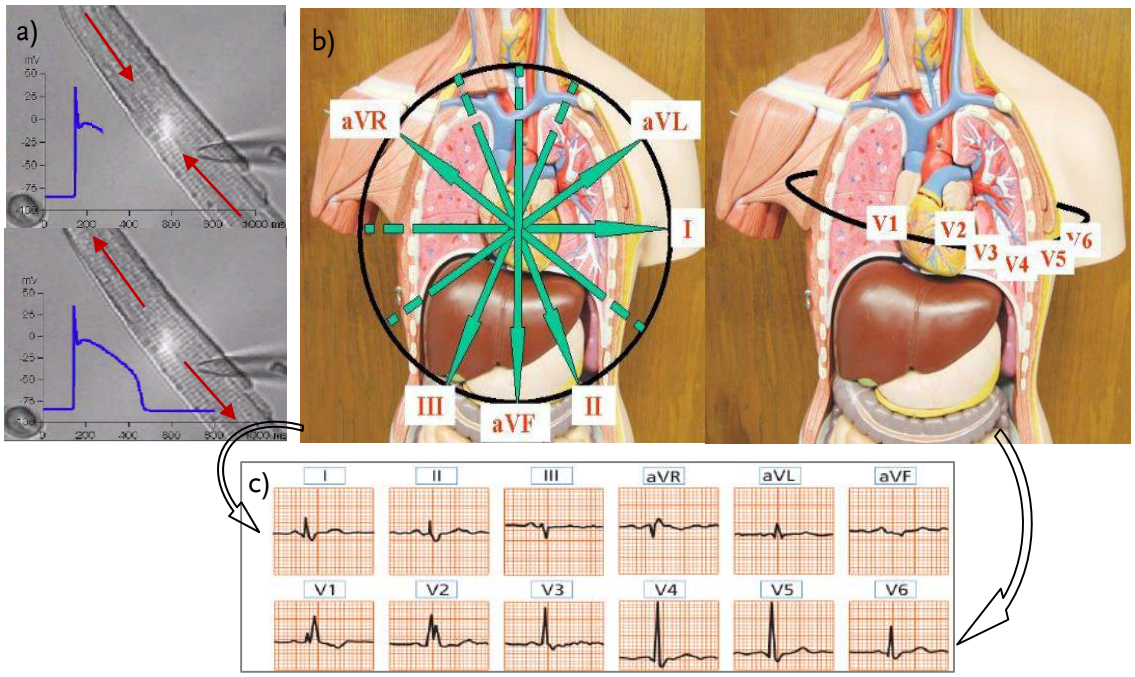


Fig. 118 – a) Contraction of a single myocardium cell and corresponding voltage variation [549]; b) In a 10 electrode setup for a 12-lead ECG, the first 6 leads (I, II, III, aVR, aVL and aVF) provide a frontal view of the heart while the following 6 (V1-V6) provide a cross sectional top view adapted from [550]; The combination of the 12 leads expose electrical abnormalities in the myocardium, in this case a blockage of one of the electrical conduction branches [544] .

The same would be done for the sound waves. From **first principles** we would see that sound waves are propagating high and low pressure zones. We would study how best to capture that propagation from the human body (which ultimately ends in the vibration of the skin). By doing this we could also **challenge the status-quo** by studying how stethoscopes work (**Fig. 119 a-b**), which we would soon discover they work as sound channels and splayers of the heart beating sounds (**Fig. 119 c**).

If this idea was to be pursued further, then the analysis wouldn't of course stop here. A deeper understanding should be pursued. When that was achieved, new constraints should have risen, and solutions should start to be explored, as the **divergent thinking** phase takes place in the ideation process that starts.

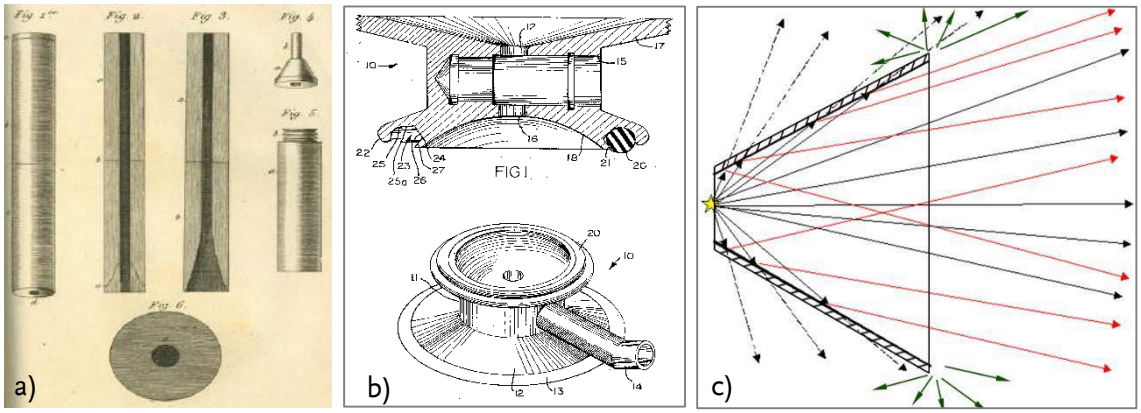


Fig. 119 – a) Drawing of an early monoaural stethoscope by Rene Laënnec in 1819 [551]; b) Patent drawing of a simple chest piece for a stethoscope [552]; c) Sound wave focusing in a megaphone. Red: reflected sound waves; Green: diffracted sound waves. The opposite effect is achieved if sound is coming from the opposite way, as in the chestpiece, see b. Adapted from [553].

It could be useful to perform a **simple language reframing**, where the problem could be reformulated in colloquial words resulting in e.g. "a device that conducts well electricity and sound for heart problems detection", making it simpler to have the whole concept in the working memory of our brains. In order to propose some solutions for the challenge, a session of **brainstorming** can then be taken.

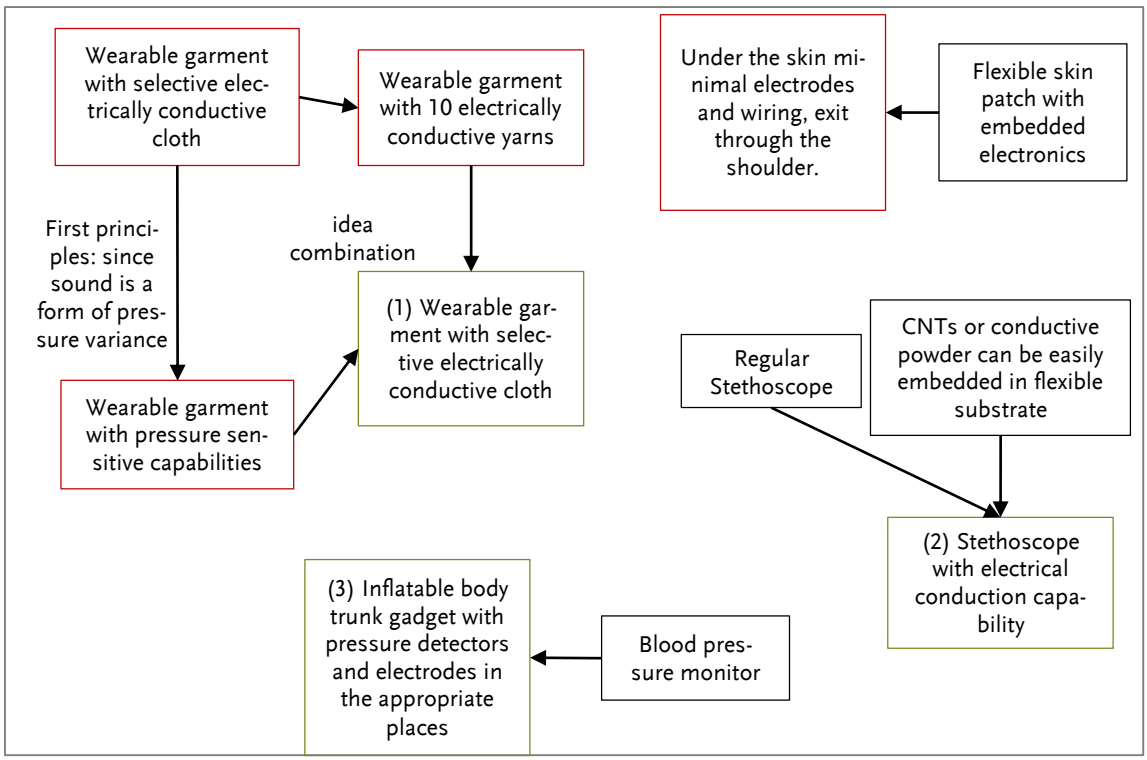


Fig. 120 – Brainstorming for ideas for the multifunctional HealthyHeart device. The arrows represent the way ideas were originated. Red rectangles contain unifunctional concepts (containing either electric or sound function), green rectangles contain multifunctional concepts.

A great number of ideas can then be suggested by the team written on a board, 'post-its' or in web-based applications such as www.stormboard.com. In this case three is not really a high amount of ideas (quantity > quality), but will be enough for the purpose of this example.

Having an amount and general quality of ideas/concepts that the team feels comfortable with to extract a great solution from, the **convergent thinking** begins[5]. Rough prototypes made of simple accessible materials and visual sketches should be created soon in the product development phase, to present a hands-on and visual testing for detection of trivial problems with the most promising concepts. In **Fig. 121** two visual sketches were drawn for the two ideas that had more potential (the inflatable device was discarded since it was deemed too impractical) containing already some initial possible design details and explaining the core functionality of the concept.

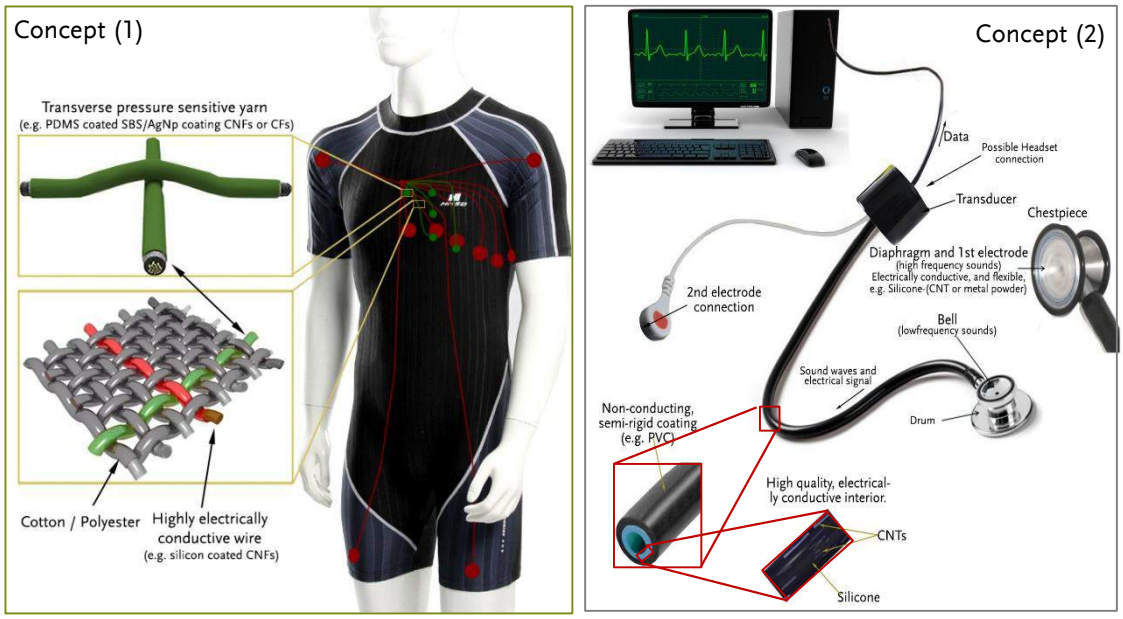


Fig. 121 – a) Wearable multifunctional underwear for heart abnormalities detection through electrical and sound analysis. Images (all adapted) from [265, 554]; b) Multifunctional stethoscope for heart abnormalities detection through electrical and sound analysis. Images adapted from [98, 555–558].

In a previous chapter it was mentioned how concurrent product and material design ought to be preferable to product design and later material selection and now it should be clear why. The reader might notice how the materials are at the core of the functions, especially in the most integrated concept (1). For instance, if the material doesn't have

[5] A note should be made by referring how these phases aren't rigid. New ideas can still be suggested in later stages, but that has the problem of slowing down progress because the team has to take some steps back in re-analyzing the new idea. For that reason, the sooner more ideas are presented the better.

energy storage capacity, there will have to be another component with it, which might drastically change how the initial product is used.

As the sketches and prototypes are done and analyzed the better concepts should become increasingly obvious. The first concept, while significantly more innovative, also should be more expensive, as it can only be used for a person. Then there's the issue of connectivity and power. Since concept 2 can be used in a physician's room, there should be access to electricity and to one computer or a portable display device, for the physician to be able to see the ECG. The first concept, could integrate solar energy harvesting fibers and energy storing fibers for powering the data storage, but that is technology a few years ahead. If, on the other hand, it ought to be connected to a power source, then the concept of 'wearable' loses its mobility advantage. Let's assume then, that concept 2 was deemed the better option for the current constraints.

When measuring voltages as low as the ones that reach the skin coming from the myocardium (mV) it is important that relative movement between the electrode and the skin is minimized so as not to introduce noise in the measurements. For this we could use some adhesion between the electrodes and the user's skin. We can turn to **inspiration from nature** by looking into how it solves similar problems (**problem-driven approach**), that is, what mechanisms do living beings use to obtain adhesion. Here an AI /web-based application as proposed before would be extremely useful to provide highly organized information about the topic. Searching in www.AskNature.com would yield results such as the gecko's feet previously mentioned. As we saw in the same chapter, some prototypes of structures that mimic the functional principle already exists, at least one of them in silicon, which is appropriate for this application, so they could be studied to assess the possibility of being included as represented in **Fig. 122**.

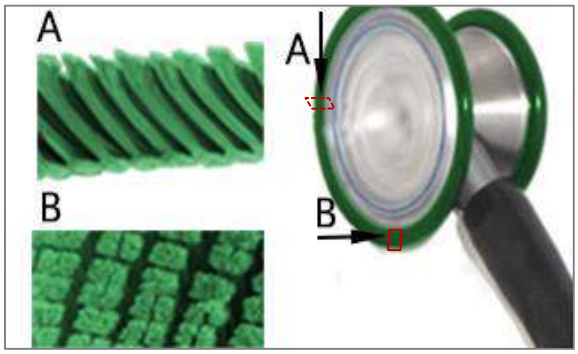


Fig. 122 – Bio-inspired (gecko's) adhesion mechanism for the chest piece rim. Images adapted from[438, 555].

In looking for ways to improve sound transmission and reception, a search in the same database would reveal interesting papers on topics such as the mammalian inner ear [559], some insects' directional hearing [560, 561] and 3D sound mapping by owls [562], which could provide a good underlying principle to be extracted, and eventually to be applied to the stethoscope.

In terms of **designing for sustainability** we could think for example whether the newly discovered electrically conductive cellulose film [513] would be suitable for the diaphragm, that is, if it reliably transmits sound waves into the stethoscope channel. In order to reduce the final costs, it could be tried to replace the CNTs with electrically conducting particles such as metallic powders. If the only viable option is to use inorganic materials, how best can materials be integrated in order to facilitate recycling?

Depending on the ability to **share** the company's or team's **knowledge**, a more collaborative approach could be pursued by using the power of **crowdsourcing** in formulating solutions for the issues that emerge.

A **performance analysis** where MFMS are used should be made, comparing it to unifunctional designs, in terms of quality of sound and electrical signal which ultimately would determine the efficacy of the product with and without a physician in correctly identifying or aiding in the identification of diseases or other abnormalities of the heart. Both sound signal and electrical quality can be evaluated using the appropriate tools [563, 564] and then compared with a regular stethoscope and electrocardiograph (**Fig. 123**).

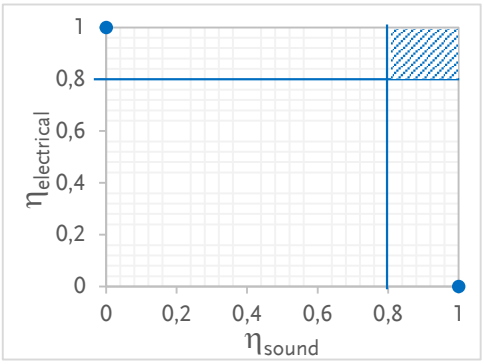


Fig. 123 – The dots represent unifunctional efficiency. Painted area represents accepted values based on a suggested minimum of 80% of efficiency for either function.

The next steps concern a typical product development as showed before such as designing the look and usability of the stethoscope, analyzing existing patents and the need to propose a new one, establishing functional diagrams, e.g. flow diagrams (**Fig. 124**), testing the several concepts proposed for the multifunctional stethoscope, and all the following steps (**Fig. 108**).

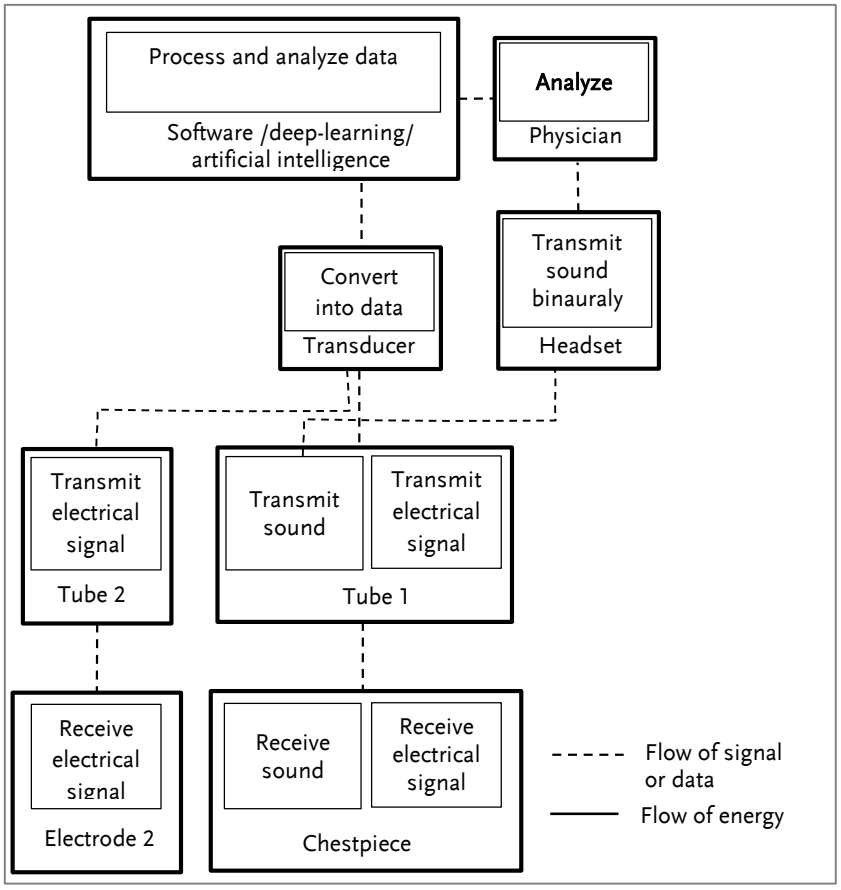


Fig. 124 – Schematic of the proposed multifunctional HealthyHeart stethoscope for analysis by AI/software and/or physician.

CHAPTER 5

Ideas for Future Work

In this chapter a few provocative, futuristic ideas are suggested for further development. I believe the development and application of MFMS to the ideas presented is susceptible of creating a great impact. They will be grouped by the field where they belong. Let's start with Civil Engineering.

5.1 For Civil-Engineering Applications

Below is a list of interesting properties in addition to good static mechanical properties that, due to their usefulness, future civil engineering structures will certainly have and that most likely will incorporate MFMS:

- Homeostasis [565] – The biological principle of homeostasis states that when an external agent interacts with a homeostatic structure it changes intelligently, for example shape, so that it regains its load bearing capacity. For example, if a homeostatic chair would lose one of its legs, it would rearrange the remaining three in order to be positioned as a tripod. This principle could be extrapolated to not only apply to structural but also to other functions. For example, a material that has a certain electrical conductivity at a certain temperature, might self-regulate its internal temperature in order to maintain the optimum electrical conductivity;
- Cooling/Heating regulation, e.g. [566];
- Self-monitoring;
- High UV and humidity resistance;
- Multifunctional windows including color, transparency [567, 568] and selective air circulation from the outside [569];
- Transparent structural materials to minimize the visual impact of structures (**Fig. 125 a**);
- Ability to incorporate microorganisms to perform functions such as air-cleaning and temperature regulation (**Fig. 125 b**);

- Roads with dynamic (changing) embedded displays. A starting point has been the glow in the dark roads in the Netherlands [570] (**Fig. 125 c**);
- Energy-polyvalent structures: integrated energy harvesting and storing, internet signal emitter, charging station, etc. (**Fig. 125 d-e**).

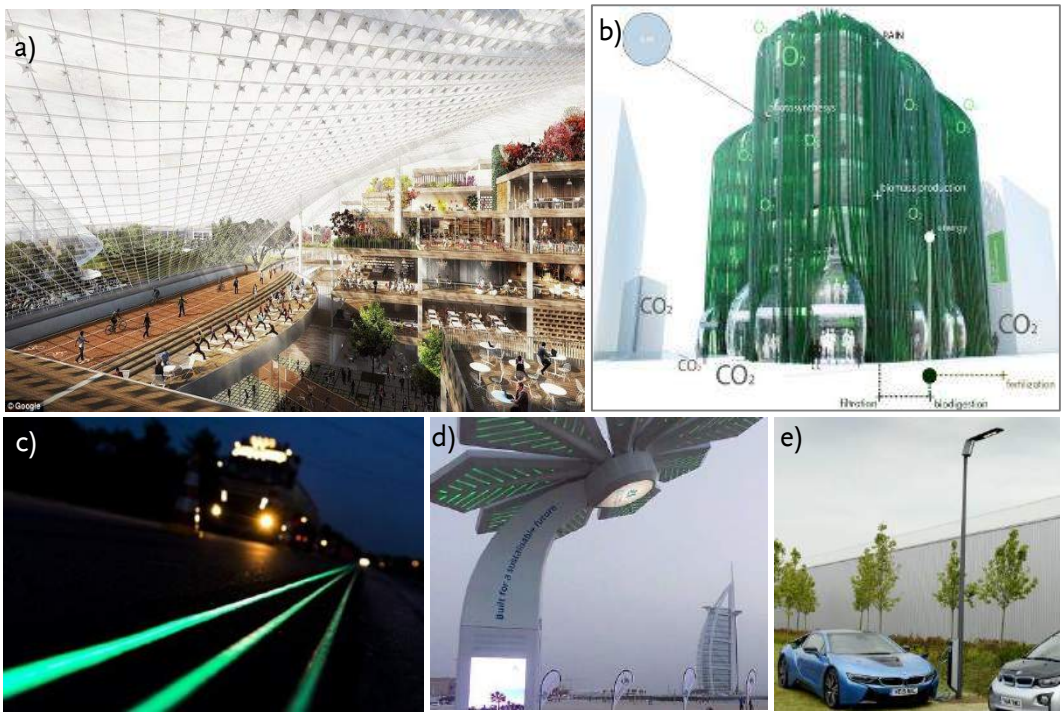


Fig. 125 – a) Tented city project by Google [571]; b) A bio-digital cladding system by ecoLogicStudio [572]; c) Glow in the dark markings in a portion of a road in the Netherlands [570]; d) The multifunctional SmartPalm in Dubai [573]; e) Street lightning system with integrated vehicle charging being developed by BMW [574].

5.2 For Medical Applications

There is quite a wide range of possible medical applications for MFMS. There is a huge amount of parameters to be measured and treatments to be delivered, which certainly require multifunctionality by the system that is responsible for them. In the following paragraphs a few opportunities for MFMS are presented.

The BiVACOR heart currently seems to be the most promising artificial heart [575] (**Fig. 126 a**). It has been successfully transplanted to a live sheep and can last more than 5 years. It only has 1 moving part, a turbine, and therefore has no beating mechanism. It is small enough that can fit in children but powerful enough for adults. However it still needs rechargeable li-ion batteries. If it could draw power directly from the body it would be completely autonomous. This fits in with the energy harvesting material systems that are being developed for the same function, mentioned in the chapter Energy Harvesting Possibilities.

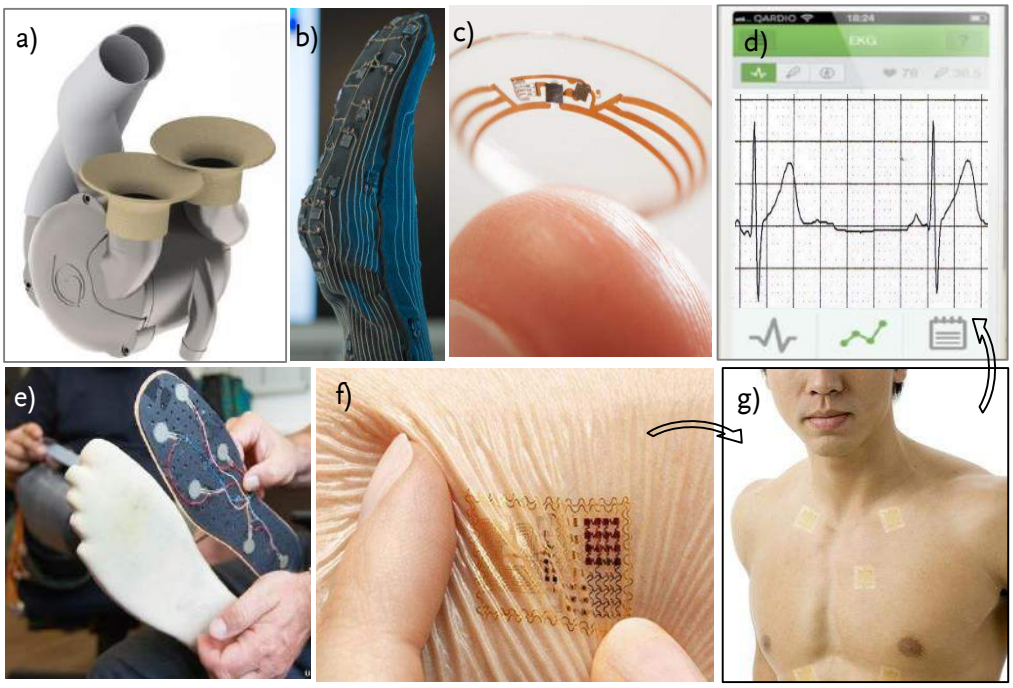


Fig. 126 – **a)** A 3D rendering of the BiVACOR heart [575]; **b)** Pressure-monitoring socks with embedded elastomer sensors without the exterior textile layer. Exhibited at the 2015 SENSOR+TEST trade fair in Nürnberg [576];**c)** Google's smart lens concept for blood glucose measuring[577]; **d)** QuardioCore iPhone application for the wearable ECG ECK monitor adapted from [578]; **e)** Artificial foot with pressure sensors that give sensing feeling to the user [579]; **f)** A flexible skin patch with embedded electronic circuits that will be one of the many that one day will provide several sensing abilities for continuous human health monitoring [580]; **g)** Man:[581], electrodes: [582].

Diabetics can't properly detect pressure and temperature in their feet which can result in wounds and abscesses. Some researchers are developing a wearable sock with pressure sensors that send a warning when pressure is too high or for long periods of time so that the wearer can shift weight [576]. The image (**Fig. 126 b**) shows the product at a trade fair demonstrator without its second, external textile layer.

A similar concept was developed by Austrian scientists [579] that consists of the base of an artificial foot which has sensors that are connected to an amputee's nerve endings giving him the sensation of feeling in that artificial foot **(Fig. 126 f**). It's possible to see that in both cases, higher integration of the pressure sensors with the textile would be possible, and also a higher density of them. Would ZnO nanowires or a CNT thread coated with a non-conducting material woven into the sock's material allow such pressure sensitivity? The idea would be that their piezoimpedance would be changed when strained, making it possible to locate and quantify the strain. If such was possible it would allow for far greater resolution of sensitivity.

Finally, there's the idea of using MFMS to create 24h health monitoring. Health monitoring has been increasing both in frequency and quality. From never getting our health checked, during pre-historic, times to the current days where we usually only check our health for a few routine checkups ranging from once or twice every year to once a few years, or when symptoms occur, if the trend maintains then the likely direction is 24h

health monitoring. I foresee a future where for example our organs are under scrutiny 24/7 both being monitored and administered the treatment at the same time, if artificial organs aren't invented first, that is, but the former seems more in reach to our current technology. Still, for that to be possible we first need flexible electronics that wirelessly transmit information to a receiver which then continuously analyses the data. We're already moving in that direction [583-585], but the technology once again finds the barrier of energy harvesting being an issue. Current Li-ion batteries only have so much energy density, therefore even small structural batteries would only be suitable if the energy requirements were equally small, but this still would still require the device to be charged, which is inconvenient and not the ideal situation of a self-powered device, which is what we're trying to achieve.

As a first step, subcutaneous or cutaneous patches seem to be the easier choice to start with **(Fig. 126 f**), but later on other less visible and smaller solutions will almost certainly be used. The material system for such application should have a multitude of sensing abilities:

- Temperature – to detect infections, heat strokes or hypothermia, etc.;
- Electrical conductivity – e.g. to measure and continuously transmit all the electrical activity of the heart, as the Holter monitor does;
- Pressure – continuous measurements of blood pressure, sensitivity to sound waves coming from the beating of the heart;
- Multiple chemical sensing – possibly the hardest to achieve, as there are many biological chemicals to sense, with very distinct natures.

Finally, both of the two ideas mentioned as taking part in the example for a heart abnormality detector instrument, the multifunctional stethoscope and the wearable pressure sensitive and electrically conductive suit could reveal fruitful if further studied.

5.3 In Transportation

Transportation too, would greatly benefit from the adoption of MFMS. Take for example the design for a defensive military aircraft from BAE systems (**Fig. 128 a**) which incorporates several functions. Futuristic designs for commercial airplanes also tend to follow the same principle of civil engineering structures, which is to minimize the visual impact of the structure. For example the Ixxon's windowless private Jet which garnered the first prize in the private aviation exterior design concept at August's International Yacht and Aviation Awards ceremony in London (**Fig. 128 b-c**). In the start, multifunctionality will most likely be achieved with type 2/3 composites which makes it hard to achieve transparency because all of the layers would need to be transparent. Also, interior displays covering the entire structure would better serve entertainment purposes for the passengers, and would still allow to stream the exterior view. Would it be possible to cover less

structurally demanding parts of the skin of the aircraft with solar harvesting materials, and Sharklet ribbons to decrease drag (**Fig. 128 e**)? A tiny step towards this goal has been achived with the plane Solar Impulse which has 0 emissions because of na external layer of photovoltaic cells and is curently travelling the world promoting a cleaner future (**Fig. 128 d**).

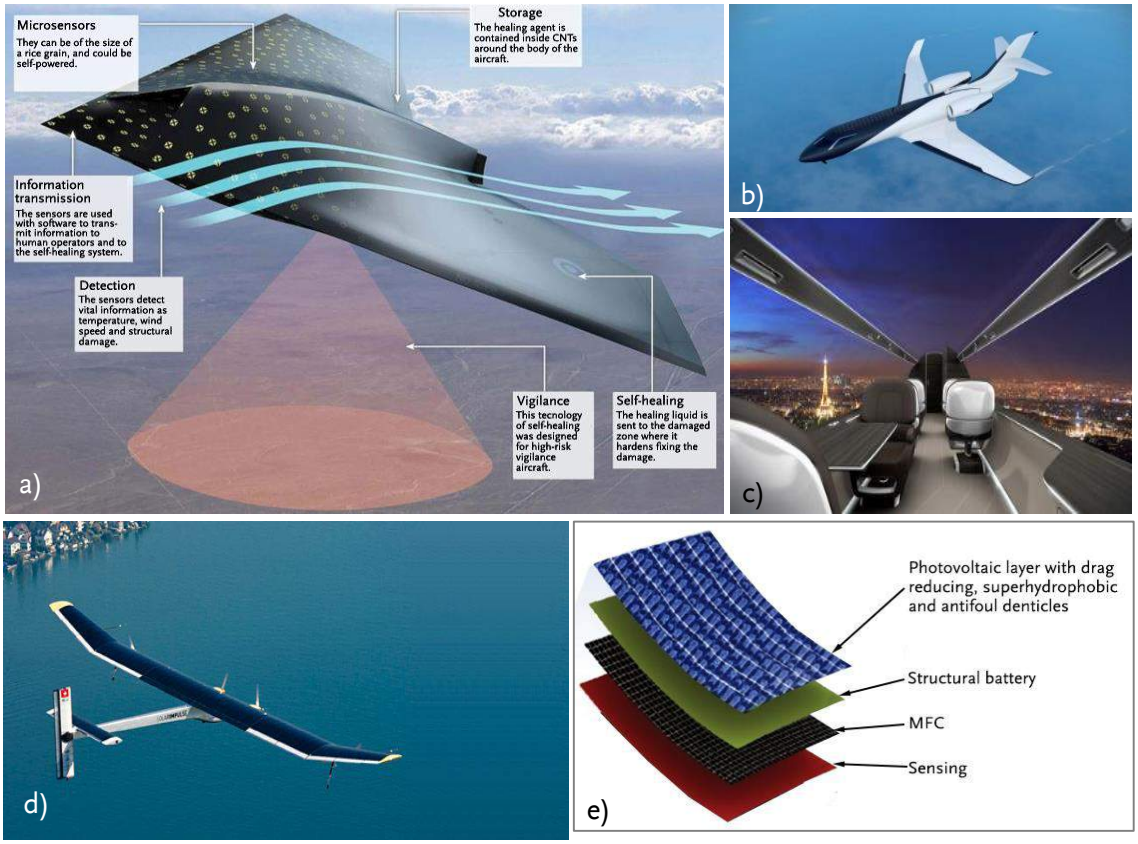


Fig. 127 – a) BAE systems design for a military aircraft, adapted from[586]; b–c) Windowless jet design, view from the outside and inside [587]; d) The first Solar Impulse, a zero emission airplane that could pave the way for future solar–powered aircraft in one of its many test flights [588]; e) Proposed multifunctional material system for an aircraft skin, based on [587].

A similar initial step has been taken with the Sunswift's eVe (**Fig. 128 a**). The first street legal solar car that recently (2014) broke the world record of speed for a solar car travelling 500km with an average speed of 114km/h [589]. Due to lower structural requirements, the same idea of a multifunctional skin (**Fig. 128 e**) could be studied.

Another perspective to look at for ground-based vehicles is energy recovery, which for the electric ones the most interesting system to recover energy from would be the breaking, suspension and rolling resistance. It's unclear whether in the future it will be necessary to recover such small amounts of energy compared to what's necessary to move the vehicle. Energy storage systems and solar energy harvesting should be improved, significantly reducing the need for such concern, and therefore the need to develop these recovery systems might not be needed at all. Nevertheless, for the former two there are already a few solutions and they involve electro-mechanical recovering systems. For the

latter, piezoelectric and thermoelectric materials could be a viable option, as the concept-tire presented by Goodyear (**Fig. 128 b**).

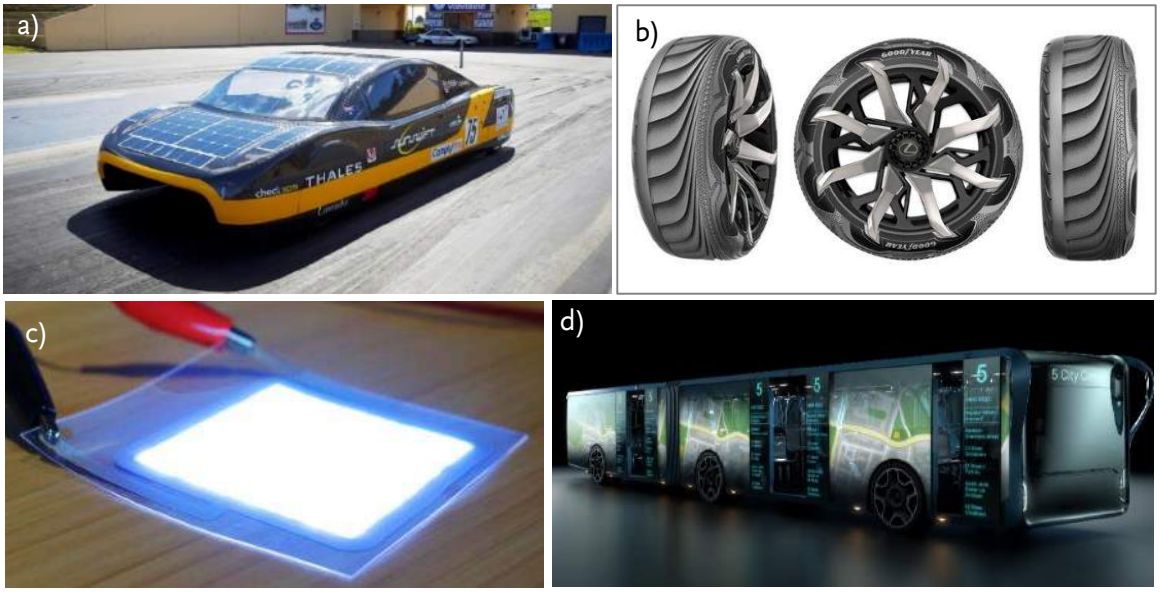


Fig. 128 – Sunswift's eVe [589]; Concept tires unveiled by Goodyear at May's Geneva International Motor Show that generate electricity by using piezo and thermoelectric materials [590]; **c)** 3D-printed thin LED[535]; **d)** Design of a bus with structural displays [591].

5.4 Helping Those in Greater Need

The three main issues that seem to prevent developing countries to advance faster are reported to be related to health, agriculture and housing, and political problems [592] (**Fig. 129**).

Salamanca et al. [593] argue that nanotechnology, category in in which they include functional materials, can help alleviate some of those issues and have ranked the applications of nanotechnology that are most likely to benefit developing countries according to a panel of 63 nanotechnology experts, of which 60% were from a developing country. The final ranking was the following list, of which a few examples most related to MFMS were selected for a better understanding of the proposed ideas:

1) Energy storage, production and conversion, e.g.
    a. Photovoltaic cells and organic light-emitting devices based on quantum dots;
    b. Carbon nanotubes in composite film coatings for solar cells;
2) Agricultural productivity enhancement, e.g.
    a. Nanosensors for soil quality and for plant health monitoring;
3) Water treatment and remediation, e.g.
    a. Magnetic nanoparticles for water treatment and remediation;
    b. TiO_2 nanoparticles for the catalytic degradation of water pollutants;

4) Disease diagnosis and screening, e.g.
    a. Nanosensor arrays based on carbon nanotubes;
5) Drug delivery systems, e.g.
    a. Nanocapsules, liposomes, dendrimers, buckyballs, nanobiomagnets, and attapulgite clays for slow and sustained drug release systems
6) Food processing and storage, e.g.
    a. Nanocomposites for plastic film coatings used in food packaging;
7) Air pollution and remediation, e.g.
    a. Nanosensors for detection of toxic materials and leaks;
8) Construction, e.g.
    a. Nanomaterials for cheaper and durable housing, surfaces, coatings, glues, concrete, and heat and light exclusion;
    b. Self-cleaning surfaces (e.g., windows, mirrors, toilets) with bioactive coatings;
9) Health monitoring, e.g.
    a. Nanotubes and nanoparticles for glucose, CO 2 , and cholesterol sensors and for in-situ monitoring of homeostasis;
10) Vector and pest detection and control, e.g.
    a. Nanoparticles for new pesticides, insecticides, and insect repellents.

All of these ideas have a common underlying problem, which is that they also tremendously benefit the developed countries, and if history is of any indication, when that happens generally the gap between the developed and the developing countries tends to widen instead of shrink [594] for example because corporations of the former tend to withhold the patents which are then put at a price tag far too expensive for governments and companies of developing countries to afford. Also, since technology related to MFMS is relatively new, and often involves expensive materials and manufacturing processes, currently MFMS tend to be expensive as well, which puts another barrier for their adoption in developing countries.

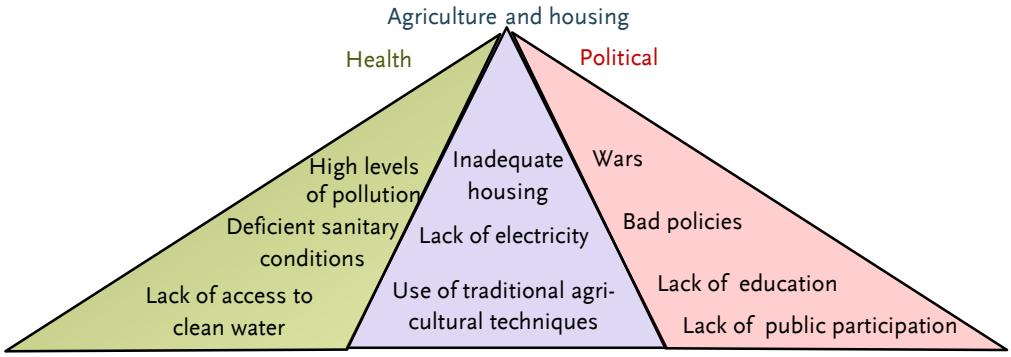


Fig. 129 – The biggest issues currently preventing a faster rate of development in developing countries.

I would argue that for a product to shrink the gap between these two types of countries, products to be developed need to solve problems that are already solved in the developed countries and which don't compete directly with their solutions.

A good example of a such a product is the GravityLight which is a cheap way of providing a source of light other than the carcinogenic kerosene that is commonly used in African countries [595] (**Fig. 130**). Powered by the conversion of potential energy of a weight to kinetic by a pulley system which then is converted to electrical which powers LEDs.

Still, the viability of using MFMS for products produced specifically to developing countries remains an uncertain future for the reasons mentioned above, but the possibility should at least be present in scientists and engineers' minds when developing these products and materials. As IDEO's founder Tim Brown mentions frequently [370], empathy is a great way to inspire new ideas. This is a really important issue that ought to be addressed if we're really calling ourselves a superior species.

Though not an ideal situation, the adoption of MFMS could still indirectly help these countries if at least part of their production was outsourced there. For example, if materials from the Growing Materials chapter would take off, why not outsource their production to these countries? This could aid in the development of their agricultural techniques, which are seriously lacking [592], by sending trained technicians to train locals while at the same time benefiting the producers by having comparatively cheap labor. Also, outsourcing manufacturing to these countries isn't a farfetched idea as evidenced by the recent surge in interest by giant manufacturers in moving their production facilities there [596-599].



Fig. 130 – A child in an African country reading under a kerosene lamp [595].

CHAPTER 6

Conclusions

A state-of-the art concerning major MFMS developments and achievements was presented along with the introduction of some nomenclature that it needed to increase clarity throughout the rest of the dissertation. It was observed that the fields related to MFMS are in clear expansion, and there are great progresses being made in all of the areas analyzed, namely CNTs, FGMs, piezoelectric materials, SMMs and others, with some emphasis on the former.

The challenges concerning existing MFMS were found to be mainly related to manufacturing, development of new and existing ones and better support for the adoption of MFMS in products. More specifically, systematization of the ideation process, analysis of performance and the product design process with these new class of highly tailorable MS, better support for sustainable products to develop, and a better interconnection between different fields of study responsible for each of the materials system's function, which includes adopting different ways to share and organize information between scientists and engineers.

Some creativity-promoting tools were then presented to help in material, structural and product innovation, as well as suggestions with the goal of promoting creativity, productivity and greater communication between people from the numerous different fields that need to work side by side.

Then it was discussed how nature can be a great source of knowledge to aid in the development of MFMS and its products. It was found that this is also a field growing at an extremely high rate. Some inspiring materials were mentioned and some case studies of successful bio-inspiration were analyzed. Then a few methods for successful biomimetics were presented, both human and artificial intelligence-based. There is a growing interest in the latter, which could someday overflow to all analogy-based design.

After this, it was analyzed where MFMS would fit in the product development process as their increased tailorability and complexity creates some opportunities for a more in-

tegrated approach between materials, structure and product development in comparison with the traditional way where materials are simply selected from an existing database based on their properties. It was argued that MFMS should be analyzed earlier in the product design process because to take full advantage of their benefits, it is beneficial to concurrently develop product and material at the same time.

Then it was suggested a few ways to develop MFMS in a sustainable way, namely by growing materials with the help of living organisms, by using natural materials, e.g. cellulose, in different ways and their role in MFMS, and how the development of these materials can help in improving energy sustainability. Major ways in which this can happen is by the harvesting of energy from unused sources of energy such as from machine vibration, the human body and structures.

The chapter was then wrapped up by synthetizing all the major ideas discussed into a scheme and in an example for a heart abnormalities detecting instrument.

Finally, some provocative and challenging ideas were left to the reader as sources of inspiration, or as future works, in civil, medical, transportation and in helping developing countries. Future applications can greatly benefit from the adoption of MFMS, so it is but a matter of us, engineers and scientists, to work with dedication and passion in order to advance this field.

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Appendix A: Physical, Mechanical and transformation properties of SMAs [218]

Table II Physical, mechanical, and transformation properties of SMAs

	NiTi	Cu-based alloys
Physical properties		
Density (g/cm^3)	6.4-6.5	7.1-8.0
Melting point (°C)	1,250	950-1,050
Thermal conductivity (W/mK)		
Martensite	8.6-10.0	–
Parent phase	18	79-120
Electrical resistivity ($\times 10^{-6}\Omega$m)		
Martensite	0.5-0.6	0.14
Parent phase	0.82-1.1	0.07
Co. thermal expansion ($\times 10^{-6}$ K^{-1})		
Martensite	6.6	16.0-18.0
Parent phase	10.0-11.0	–
Specific heat capacity (J/kg K)	470-620	390-440
Enthalpy of transformation (J/kg)	19.0-28.0	7.0-9.0
Corrosion performance	Excellent	Poor
Mechanical properties		
Young's modulus ($\times 10^9$N/m^2)		
Martensite	28-41	70
Parent phase	70-97	70-100
Yield strength ($\times 10^6$N/m^2)		
Martensite	70-140	80-300
Parent phase	195-690	150-350
Ultimate tensile strength ($\times 10^6$N/m^2)		
Martensite	895	400
Parent phase	1,900	1,000
Elongation at failure (%)		
Fully annealed	25-50	8-15
Work hardened	5-10	8-15
Hot workability	Poor-fair	Very good
Cold workability	Poor	Good
Machinability	Poor	Very good
Transformation properties		
Transformation temperature range (°C)	−200 to +120	−200 to +200
Recoverable strain (%)	8	4
Normal working stress (MPa)	180 ÷ 130	40 ÷ 70

Appendix B: 40 Inventive Principles of TRIZ[350, 600]

1. Segmentation 1.1 Divide an object into independent parts. 1.2 Make an object easy to disassemble. 1.3 Increase the degree of fragmentation or segmentation.	**21. High speed** 21.1 Conduct a process , or certain stages (e.g. destructible, harmful or hazardous operations) at high speed.
2. Removal 2.1 Separate an interfering part or property from an object, or single out the only necessary part (or property) of an object.	**22. Turning harm to good** 22.1 Use harmful factors (particularly, harmful effects of the environment or surroundings) to achieve a positive effect 22.2 Eliminate the primary harmful action by adding it to another harmful action to resolve the problem. 22.3 Amplify a harmful factor to such a degree that it is no longer harmful.
3. Local quality 3.1 Change an object's structure from uniform to non-uniform, change an external environment (or external influence) from uniform to non-uniform. 3.2 Make each part of an object function in conditions most suitable for its operation. 3.3 Make each part of an object fulfill a different and useful function.	**23. Feedback** 23.1 Introduce feedback (referring back, cross-checking) to improve a process or action. 23.2 Introduce feedback (referring back, cross-checking) to improve a process or action.
4. Asymmetry 4.1 Change the shape of an object from symmetrical to asymmetrical. 4.2 If an object is asymmetrical, increase its degree of asymmetry.	**24. Intermediary Object** 24.1 Use an intermediary carrier article or intermediary process. 24.2 Use an intermediary carrier article or intermediary process.
5. Merging 5.1 Bring closer together (or merge) identical or similar objects, assemble identical or similar parts to perform parallel operations. 5.2 Make operations contiguous or parallel; bring them together in time.	**25. Self-service** 25.1 Make an object serve itself by performing auxiliary helpful functions. 25.2 Use waste resources, energy, or substances.
6. Universality 6.1 Make a part or object perform multiple functions; eliminate the need for other parts.	**26. Optical copies** 26.1 Instead of an unavailable, expensive, fragile object, use simpler and inexpensive copies. 26.2 Replace an object, or process with optical copies. 26.3 If visible optical copies are already used, move to infrared or ultraviolet copies.
7. Nesting 7.1 Place one object inside another; place each object, in turn, inside the other. 7.2 Make one part pass through a cavity in the other.	**27. Short life** 27.1 Replace an inexpensive object with a multiple of inexpensive objects, comprising certain qualities (such as service life, for instance).
8. Anti-weight 8.1 To compensate for the weight of an object, merge it with other objects that provide lift. 8.2 To compensate for the weight of an object, make it interact with the environment (e.g. use aerodynamic, hydrodynamic, buoyancy and other forces).	**28. Mechanical replacement** 28.1 Replace a mechanical means with a sensory (optical, acoustic, taste or smell) means. 28.2 Use electric, magnetic and electromagnetic fields to interact with the object. 28.3 Change from static to movable fields, from unstructured fields to those having structure. 28.4 Use fields in conjunction with field-activated (e.g. ferromagnetic) particles.
9. Preliminary counteraction 9.1 To compensate for the weight of an object, make it interact with the environment (e.g. use aerodynamic, hydrodynamic, buoyancy and other forces). 9.2 Create beforehand stresses in an object that will oppose known undesirable working stresses later on.	**29. Pneumatics and hydraulics** 29.1 Use gas and liquid parts of an object instead of solid parts (e.g. inflatable, filled with liquids, air cushion, hydrostatic, hydro-reactive).
10. Preliminary action 10.1 Perform, before it is needed, the required change of an object (either fully or partially). 10.2 Pre-arrange objects such that they can come into action	**30. Membranes** 30.1 Use flexible shells and thin films instead of three dimensional structures.

from the most convenient place and without losing time for their delivery.	30.2 Isolate the object from the external environment using flexible shells and thin films.
11. Mitigate before use 11.1 Prepare emergency means beforehand to compensate for the relatively low reliability of an object.	**31. Porous materials** 31.1 Make an object porous or add porous elements (inserts, coatings, etc.). 31.2 If an object is already porous, use the pores to introduce a useful substance or function.
12. Equipotentiality 12.1 In a potential field, limit position changes (e.g. change operating conditions to eliminate the need to raise or lower objects in a gravity field).	**32. Color changes** 32.1 Change the color of an object or its external environment. 32.2 Change the transparency of an object or its external environment.
13. Other way around 13.1 Invert the action(s) used to solve the problem (e.g. instead of cooling an object, heat it). 13.2 Make movable parts (or the external environment) fixed, and fixed parts movable. 13.3 Turn the object (or process) 'upside down'.	**33. Homogeneity** 33.1 Make objects interacting with a given object of the same material (or material with identical properties).
14. Spheroidality 14.1 Instead of using rectilinear parts, surfaces, or forms, use curvilinear ones; move from flat surfaces to spherical ones; from parts shaped as a cube (parallelepiped) to ball-shaped structures. 14.2 Use rollers, balls, spirals, domes. 14.3 Go from linear to rotary motion, use centrifugal forces.	**34. Discarding and regenerating** 34.1 Make portions of an object that have fulfilled their functions go away (discard by dissolving, evaporating, etc.) or modify these directly during operation. 34.2 Conversely, restore consumable parts of an object directly in operation.
15. Dynamics 15.1 Allow (or design) the characteristics of an object, external environment, or process to change to be optimal or to find an optimal operating condition. 15.2 Divide an object into parts capable of movement relative to each other. 15.3 If an object (or process) is rigid or inflexible, make it movable or adaptive.	**35. Change physical state** 35.1 Change an object's physical state (e.g. to a gas, liquid, or solid.) 35.2 Change the concentration or consistency. 35.3 Change the degree of flexibility. 35.4 Change the temperature.
16. Partial or excessive actions 16.1 If 100 percent of an object is hard to achieve using a given solution method then, by using 'slightly less' or 'slightly more' of the same method, the problem may be considerably easier to solve.	**36. Phase transitions** 36.1 Use phenomena occurring during phase transitions (e.g. volume changes, loss or absorption of heat, etc.).
17. Another dimension 17.1 To move an object in two- or three-dimensional space 17.2 Use a multi-story arrangement of objects instead of a single-story arrangement. 17.3 Tilt or re-orient the object, lay it on its side. 17.4 Use 'another side' of a given area.	**37. Heat expansion** 37.1 Use thermal expansion (or contraction) of materials to achieve a useful effect. 37.2 Use multiple materials with different coefficients of thermal expansion to achieve a useful effect.
18. Mechanical Vibration 18.1 Cause an object to oscillate or vibrate. 18.2 Increase its frequency (even up to the ultrasonic). 18.3 Use an object's resonant frequency. 18.4 Use piezoelectric vibrators instead of mechanical ones. 18.5 Use combined ultrasonic and electromagnetic field oscillations.	**38. Enrich** 38.1 Replace common air with oxygen-enriched air. 38.2 Replace enriched air with pure oxygen. 38.3 Expose air or oxygen to ionizing radiation. 38.4 Use ionized oxygen. 38.5 Replace ozonized (or ionized) oxygen with ozone.
19. Periodic Action 19.1 Instead of continuous action, use periodic or pulsating actions. 19.2 If an action is already periodic, change the periodic magnitude or frequency. 19.3 Use pauses between impulses to perform a different action.	**39. Inert** 39.1 Replace a normal environment with an inert one. 39.2 Add neutral parts, or inert additives to an object.
20. Continuity of useful action 20.1 Carry on work continuously; make all prts of an object work at full load, all the time. 20.2 Eliminate all idle or intermittent actions or work.	**40. Composite materials** 40.1 Change from uniform to composite (multiple) materials.