High deformation multifunctional composites: materials, processes and applications

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Abstract

Structural health monitoring (SHM) is a non-destructive process of collecting and analysing data from structures to evaluate their conditions and predict the remaining lifetime. Multifunctional sensors are increasingly used in smart structures to self-sense and monitor the damages through the measurements of electrical resistivity of composites materials.

Polymer-based sensors possess exceptional properties for SHM applications, such as low cost and simple processing, durability, flexibility and excellent piezoresistive sensitivity. Thermoplastic, thermoplastic elastomers and elastomer matrices can be combined with conductive nanofillers to develop piezoresistive sensors. Polymer, reinforcement fillers, processing and design have critical influences in the overall properties of the composite sensors.

Together with the properties of the functional composites, environmental concerns are being increasingly relevant for applications, involving advances in materials selection and manufacturing technologies, In this scenario, additive manufacturing is playing an increasing role in modern technological solutions. Stretchable multifunctional composites applications include piezoresistive, dielectric elastomers (mainly for actuators), thermoelectric, or magnetorheological materials [1]. In the following, piezoresistive materials and applications will be mainly addressed based on their increasing implementation into applications.

1. Introduction

From small to large structures, there has always been a need to monitor the structural health of the structures. Structural health monitoring (SHM) can be defined as a process to detect and quantify damage in the whole structure in order to avoid unpredicted failures that compromises the structure [2]. Ideal systems of SHM should detect and communicate damage in the structures, allowing intervention to correct the affected damage, or in extreme cases, to avoid a catastrophe, such as the collapse of a building or a bridge.

Sensor networks can detect anomalies or small variations in the structure, avoiding propagation of failures in order to improve reliability and reduce life-cycle costs [2]. During the last decades, the large-scale infrastructures (typically civil building or bridges) have been increasing the dimensions of the construction. Evaluate the structural health condition of structures during their long-term service life, to ensure its serviceability and sustainability, is essential, being sensor networks a need to monitor structures in real time.

For each specific structure, it is necessary to evaluate the SHM design to detect the critical variations on the structure in order to select the sensor type and precision that is required to evaluate the structure and their failures. Monitoring the characteristics of damage in a particular structure plays a key role in defining the architecture of the SHM system [2]. Force, pressure/bending, strain, temperature, or humidity monitoring are among the most typical quantities to be evaluated.

Lightweight structures are typically based in composites materials: a combination of two or more materials with novel properties that cannot be achieved by individual materials alone. Depending the final purpose of the composites, they are mostly composed by a host matrix and one (or more) reinforcing materials. The reinforcement materials are used to improve the mechanical properties or add novel properties to the host matrix, such as morphological [3] electrical [4], dielectric [5], chemical [6], magnetic [7] or thermal [8] properties.

Lightweight structures for sensing properties purposes are used in aeronautic, aerospace, naval or civil engineering components [9]. SHM devices should be capable of, in real time, monitoring and detecting structural damage at the initial phase, before a defect reaches a serious level of structural failure [9]. Additionally, the SHM systems should allow non-destructive evaluation and to be marginally invasive to the host structure [9]. A typical SHM setup is composed of a sensor (or a sensor network), a data acquisition and storage module and a damage detection algorithm, which is usually linked to a digital signal processing unit [9].

In the last two decades several approaches for SHM detection have been proposed, such as acoustic emission [10], lamb waves [2, 11], fibre optic sensors [12, 13], and eddy currents [14]. Electrical resistance variation principle is one of the most applied nowadays, such as strain gages, accelerometers, and displacement sensors. These types of sensors can be attached or embedded into the materials to monitor and determine the real-time state of the structure. They can be joined to the structure's surface, and consequently being affected by the adverse environment weather conditions, or incorporated within the materials [15].

Composites based in polymers as host matrices and reinforced with conducive nanofillers are widely used nowadays for piezoresistive sensors. Mechanical and chemical properties are provided by the polymer and electrical performance by the reinforcement fillers. The piezoresistive effect (resistance variation in response to an external applied mechanical stimulus) has been widely studied for conductive filler-polymer composites and conductive polymer-polymer blends [16] from small (<1% [16, 17]) to large strains (>100% [18, 19]) resulting in gauge factors larger than 100 [18-20] in response to the deformation.

2. High deformation piezoresistive polymers

Functional polymer-based piezoresistive materials can be achieved in all types of polymer matrices (thermosetting, thermoplastics and elastomers) reinforced with electric conductive fillers [21] or intrinsic conductive polymers (ICP) [22, 23].

High deformation functional materials should have as host matrix an elastomeric polymer and the reinforcement material can be a conductive filler, mainly nanosized fillers due to the lower impact in the mechanical properties for low filler concentrations [24], or blends with ICP [25].

The application of soft and highly stretchable materials is having an exponential growth in recent years in different area, such as electronic (soft sensing or conductive electrodes) [26], organic/inorganic conductive materials [25], harvesting [27], mechanical sensing [16, 22, 27] or dielectric applications [5], among others.

2.1. High deformation polymers

The flexibility is the main intrinsic characteristic of polymer when compared with other materials, but high deformation polymers is a subclass of these materials, usually known as elastomers or rubbers, that enable reversible large deformations [28]. The mechanical properties of the elastomeric polymers is very different from the ones of thermoplastics or resins (as shown in Figure 1), and exhibit both viscous and elastic characteristics under deformation conditions [28]. Pure elastic materials present no hysteresis effect under strain, unlike viscoelastic materials, as shown by the stress-strain characteristics of both materials. Thermoplastic elastomers and rubber-like materials are nowadays an important polymer class and their use is expected to strongly increase, reaching to 6.7 million metric tons in 2019 [29]. Figure 1 shows the mechanical stress-strain characteristics of hard and soft polymer materials.

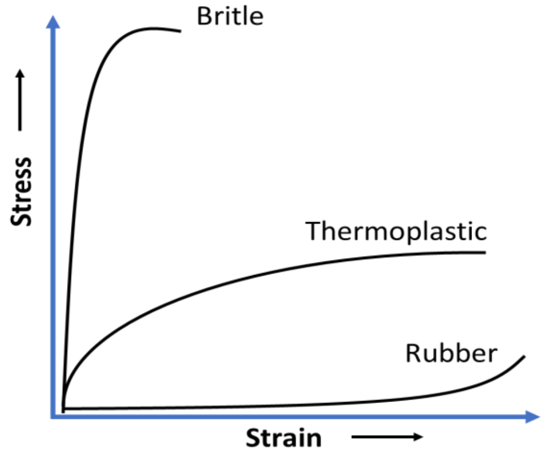

Figure 1- Mechanical stress-strain characteristic behaviour of the different polymer types: brittle, thermoplastics and rubbers.

2.2. Rubber-like Polymers

Rubber-like polymers are defined as a special type of elastomer, that is capable of retracting, to less than 1.5 times its original dimension after being stretched to twice its length [30]. A right elastomeric state with retraction even after stretching for a long time, is often only accomplished if the polymeric chains are crosslinked, for example by vulcanisation [30]. The name rubber refers to vulcanised natural rubbers (NR) or synthetic rubbers (SR), where the NR materials are produced through milky sap (also known as latex) of various tropical plants, especially of the Brazilian rubber tree Hevea brasiliensis [30]. The chemical structure of Hevea rubber is entirely cis- 1,4-polyisoprene [31]. The different types of rubber-like materials are described in Table 1.

Table 1- Classification of rubber-like materials [32].

Type	Components		Structure
	Soft	Hard	
Polyvinyl plastics	Plasticizer	Polyvinyl Chloride or Ethylene-vinyl acetate copolymer	Swollen polymer
Polyurethanes	Polyether glycol or Polyester glycol	Methylene	$(AB)_2$
Polyether esters	Polyester glycol	1,4-Benzene dicarboxylic acid	$(AB)_2$
Styrene copolymers	Polyolefin	Polystyrene	ABA
TPEs	Ethylene Propylene or Natural Rubber	Propylene or Polyethylene	Physical blend

Besides elastomer materials there are thermoplastic elastomers (TPEs) that present similar mechanical properties but no need vulcanization [16], being the vulcanization process costly and time consuming.

2.3. Thermoplastic Elastomers

Thermoplastics elastomers are a class of polymer that combine the flexibility of the rubbers and the chemical stability of the thermoplastics. TPEs are based on microphase-separated networks of soft and hard phases. The thermoplastic part acts as the hard phase (crosslinks) and the rubber-like part provides the chain flexibility and mobility [29]. Near about 70% of rubber-like polymers are used in the tyres industry, 10% in shoes industry and engineering products and about 10% in mechanical goods, being the remaining for other applications [33].

Examples of TPEs are polyurethanes (TPU), polyester elastomers, natural rubber (NR), styrene-butadiene rubber (SBR), styrene triblock copolymers ((styrene-butadiene-styrene, SBS), (styrene-ethylene/butylene-styrene, SEBS) or (styrene-isoprene-styrene, SIS) [25, 29]. Another largely used polymer is polydimethylsiloxane (PDMS), that typically consists of chemical crosslinks that are thermosets, although in certain cases a PDMS can form the soft block of a TPE, resulting in a stretchable polymer [29]. PDMS has excellent mechanical properties such as stretchability and resistance to high temperatures, to UV degradation and chemical attack [34]. PDMS has a wide range of applications such as in electrical devices, sealants and adhesives, as well as in biomedical applications [34]. Styrene triblock copolymers are known for their microphase separation into soft (butadiene) and hard (styrene) domains, with distinct morphologies [35]. SBS was first manufactured as a TPE of styrene via anionic polymerization. SEBS , a variation of SBS, shows a better oxidative stability, allowing wide range of applications, including in the biomedical area [35, 36]. Natural rubber is an important rubber widely used in industry (tyres and seals, for example) with unique mechanical properties [37]. The SBS-family has higher working range temperature and improved solvent resistance than butadiene-based rubbers [38]. SIS copolymers are similar to the SBS-family, exhibiting both elastic behaviour and thermoplastic properties [39]. Polystyrene (PS) groups that are dispersed throughout a network of rubbery polyisoprene (PI), provide the SIS structure with elasticity and the recovery properties of isoprene [39]. SBR is used for numerous applications such as tires, footwear, belts and other industrial products [40]. Similar to other rubber materials and unlike styrene triblock copolymers, SBR is vulcanized to form covalent crosslinks between polymeric chains to produce a three-dimensional network. Vulcanization causes deep chemical changes that increase elasticity and reduce plasticity [40]. TPU is also a very used TPE, comprising hard (isocyanate) and soft (polyols) segments, having been synthesized for the first time almost a century ago [41]. It has exceptional properties like elasticity, high impact and tensile strength, resistance to abrasion and weathering, excellent gloss and corrosion resistance properties, making them a good candidate for numerous applications, such as: foams, elastomers, adhesives and coatings [41]. However, under severe conditions PU alone fails to give satisfactory mechanical, thermal and corrosion resistance performance [41].

3. Conductive reinforcement materials

Research on nanoparticles to reinforce and provide novel properties to polymer composites materials has been extensively performed in the last decades. There is a large variety of metal and non-mental materials and intrinsically conductive polymers that have been used to reinforce polymers. These include metallic nanoparticles and nanowires (silver, gold, aluminium or copper), nanocarbonaceous materials such as carbon nanotubes (CNTs), graphene (G) structures, and intrinsic conductive polymers such as polyaniline (PANI), polypyrrole (PPY) and poly(3,4-ethylene dioxythiophene) (PEDOT). Thus, polymer composites can combine the best properties of the polymer with the electrical and mechanical properties of the reinforcement fillers.

3.1. Carbon nanofillers

Micro- and nanocarbonaceous materials are nowadays the most used reinforcement material.

Carbon black (CB) is among the most used reinforcement materials. CB is usually formed from thermal decomposition of hydrocarbons in the gas phase as small particle size carbon pigments [42]. The conductivity of CB is $\sigma \approx 5\times10^{-2}$ S/cm [42], it shows a graphitic structure and due to its geometry has a high specific surface area [43]. It is widely used in the rubber industry for tires, mechanical goods and in the plastic industry it is used for developing antistatic materials [42].

Carbon fibres (CFs) were used for the first time in XIX century and their size is in the micrometre range, while carbon nanofibers (CNFs) are in the nanometer size [42]. Currently, composites materials reinforced with CNFs are extensively applied in many fields [44]. The CNFs production for commercial use began in 1970's due to their interesting properties such as low density, high tensile modulus and strength or high thermal conductivity [45].

Carbon nanotubes (CNTs) were developed in 1991 by Iijima [45]. The main types of CNT include single- and multi-walled carbon nanotubes (SWCNTs and MWCNTs), respectively. CNTs can appear in three different structural forms: chiral, zigzag and armchair [46]. Their overall properties depend on the structural arrangement of the CNTs, and for example, can be conductor or semiconductor [46]. The theoretical properties of CNT are a Young modulus of 1-1.4 TPa, thermal conductivity larger than 3000 W/mK and electrical conductivity of $\sigma \approx 106$ S/cm [42]. CNTs are one dimensional (1D) carbon materials with large aspect ratio (length/diameter ratio) higher than 1000, with diameter ranging from few to some tens on nm, and a length between few hundreds of nm to some μm.

Graphene is a two-dimensional (2D) graphite with an atomic single layer, having been predicted in 1947 and experimentally realized three decades later [47]. In 2004 was rediscovered and characterized by Geim and Novoselov [47, 48]. Graphene is obtained from the exfoliation of graphite. It is also produced by chemical vapour deposition (CVD), leading to high quality graphene [48]. Single-layer graphene shows exceptional properties, including mechanical properties (Young modulus near 1 TPa), high conductivity, $\sigma \approx 6000$ S/cm, large specific surface area (2630 m^2/g) and thermal conductivity near 5000 W/(m.K) [42]. Graphene oxide (GO) and reduced graphene oxide (rGO) are the most used graphene materials. rGO shows high electrical conductivity and is also biocompatible [49].

These are some of nanocarbonaceous materials used in commercial applications. There are others carbon materials with interesting overall properties but without applications in the market. Polymer composites reinforced with nanocarbonaceous fillers have increased abruptly in the last two decades, as well the potential applications for these type of materials.

3.2. Metallic nanofillers

Nanostructured conductive materials are another way to tailor elastomeric nanocomposites to have functional conductive properties. Nanoparticles and nanowires are two of the most used nanomaterials, but there are others types of structures, including nanorods, nanocubes or nanocages [49, 50].

Silver, gold, cooper and other metallic nanoparticles- dot (0D) or wires (1D)- are currently studied to be used is specific devices, such as in naonomotors, nanorobots or nanomachines, among others, exploring various functionalities and applications [50].

Silver nanowires (AgNWs) are among used materials with easy, scalable and reproducible synthesis, having a diameter and length typically about 10-200 nm and 5-100 μm, respectively [51]. Low percolation (lower than 0.5 vol%) and transparent composites (to replace expensive indium tin oxide electrodes, for example) are two of the most technological topics addressed for a wide range of industrial areas. The reported electrical resistance of AgNWs range between 1 to 100 Ω/sq with optical transmission in composites larger than 80% [52].

Gold nanoparticles (AuNPs) are extensively studied in medical and biological applications due to their high electrical conductivity, low cytotoxicity, and biocompatibility [49]. Their diversity of geometries can be used for diagnosis, molecular imaging, and stem cell tracking [49]. AuNWs present high conductivity and optical transparency, 15 Ω/sq and 78%, respectively, with larger aspect ratio (greater than 1000, with ≈0.5 nm of diameter and ≈500 nm of length) [46].

Cooper nanowires (CuNWs) are another often used conductive nanomaterials. It is cheaper than AgNWs and can be synthetized using different methods [46], but it is also less conductive near 35 Ω/sq and can lead to 80% of transparency [53]. CuNWs with ≈100 nm diameter and length of ≈50 μm h was firstly synthesized in 2005 [54].

There are some other metallic nanowires and nanoparticles leading to composites with high conductivity and transparency [46], but the main applied materials are the ones presented before.

3.3. Conductive polymers

Since the discovery of polyacetylene, conducting polymers have become the main focus of interest for research and applications, based on their versatile electrical and optical properties [41, 55].

Polyaniline (PANI) is a conductive polymer from aniline and exists in different forms depending on its oxidation level. Pernigraniline, emeraldine, and leucoemeraldine are some forms of PANI, for completely oxidized, half-oxidized and reduced bases, respectively [49]. Emaraldine in oxidative state can be conductive and is the most stable and interesting form. PANI shows good stability, is cost efficient and can be either electrically conductive or resistant, depending on the doping level. The conductivity of the doped PANI can reach 200 S/cm in the form of nanorods or microfibrils [8, 55]. PANI is widely used in composites or blends for smart engineering applications [22, 55, 56].

Polypyrrole (PPy) is a well-known conductive polymer with appropriate chemical stability and large specific surface area [49]. Stimulus-responsive properties in vitro and in vivo and biocompatibility make PPy an excellent candidate in medical applications [49, 55]. The intrinsic conductivity of PPy ranges from 100 to 7.5000 S/m [55] and can be processed with large surface area and tailored porosities, allowing also chemical functionalization to meet specific application requirements [55].

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is another widely studied conductive polymer [52]. PEDOT is formed by the polymerization of the bicyclic monomer 3,4-ethylenedioxythiophene. The conductivity of PEDOT:PSS ranges between 1-1000 S/m and has been continuously improved [52].

4. Functional materials for structural health and biomechanical monitoring

Structural health monitoring (SHM) systems represent an area of growing interest for aerospace, civil and mechanical engineering sectors and are recognized as a powerful tool to assesses the state of structural health and predict the remaining life of the structures. The aging of existing structures and their cost of maintenance and repairs represent major concerns of engineering communities that can be solved or alleviated through SHM systems, resulting in significant savings by avoiding unnecessary maintenance or replacement [57, 58]. The primary goal of SHM is to replace the current maintenance cycles with continuous monitoring systems. Commonly, the SHM methods use micro-strain sensors able to capture strain variations due to piezoresistive and piezoelectric effects, capacitance variations, resonance monitoring or optical property changes. In this context, piezoresistive composite materials can provide a wide scope of sensors for real-time monitoring of structures and systems health, including even potential damage. Flexible and stretchable piezoresistive sensors operate based on the principle of strain variations proportionality to electrical resistance variations, transducing mechanical stimuli into electrical signals, thus representing a simple and useful tool in the field of structural health/damage monitoring, human motion detection, and personal healthcare, among others [59-61].

The monitoring of large structures as airplanes, boats, bridges and buildings usually demands sensors with high GFs and large strain measurement capabilities. Sensors may be attached to the structure to monitor them or embedded directly into the material, in order to determine the internal conditions of the structure and detect any hidden issues, determining its real-time state. The widespread use of carbon-fibre and glass-fibre reinforced composites in aerospace, automobile and naval industries strengthens the need to monitor the health of these structures, particularly in laminated composites, which in the case of outside aircraft applications, their monitoring is highly recommended. An interesting option towards SHM integrated capabilities is taking advantage of the electrical properties of these carbon-based composites for self-damage sensing, thus combining mechanical reinforcement with the sensing functionality [62, 63]. The demand and production of self-sensing systems has been growing and reports describing the manufacture of these multifunctional systems have increased so that thermoplastic and thermosetting piezoresistive polymers are expected to provide the next generation of smart materials for SHM to the aerospace, automotive, and energy industries. Particularly relevant will be the application of thermosetting polymer materials with self-sensing ability in fibre-reinforced hierarchical composites for industries demanding high load bearing capacity [64].

In this sense the concept of SHM with embedded sensors has been attracting the scientific community and several approaches have been studied, such as the dispersing of high aspect ratio CNFs into epoxy resin matrix by mechanical stirring, which resulted in a noticeable stable and repeatable piezoresistive response, under several types of cyclic loadings, achieving GF≈ 56 for 1.16 vol% of CNFs into the polymer matrix (Figure 2) [65].

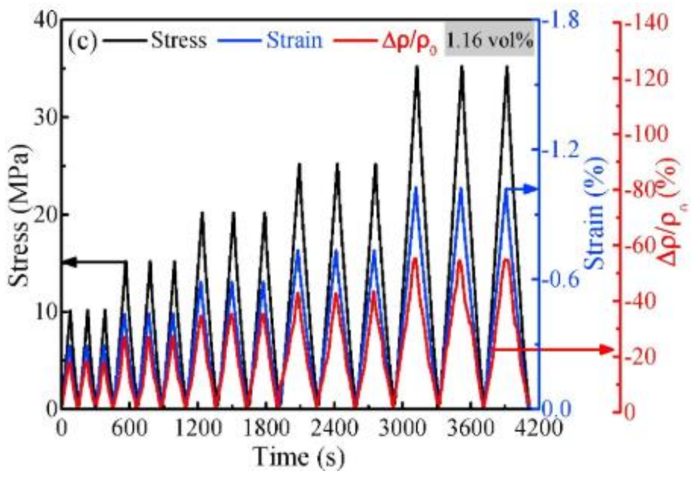

Figure 2: Typical relationships between relative change in resistivity and the incremental cyclic compressive strain/stress for epoxy composites filled 1.16 vol% of CNFs [65].

These composites present at the same time enhanced mechanical/structural properties, such as compressive strength and the elastic moduli, and the possibility of being used as compressive strain sensors for SHM [65].

Reinforced laminated composites of epoxy resins with glass fibre were functionalised with an uniform coating of rGO, obtained by electrophoretic deposition of GO, and beyond the mechanical enhancement achieved on the dynamic elastic moduli, flexural strength and delamination resistance, the composites showed electrical resistivity in the range of 10^{-1} Ω/m, which allowed a good piezoresistive behaviour under flexural condition thus demonstrating suitability for strain/damage monitoring. The strain sensitivity of the system increased for higher temperatures, which shows its usefulness in structural applications subjected to high service temperatures conditions [66]. With view in the development of embedded sensors for aeronautic structural applications, epoxy-based composites filled with 0.3 wt% of MWCNTs were produced and their piezoresistive response assessed by DC and AC measurements in axial and flexural strain modes. From the electromechanical characterization resulted that the AC operation at 1 MHz revealed an improved sensitivity, about 2 orders of magnitude higher than in DC mode, as well as high reliability and reversible response, meaning a consistent path towards self-diagnostic functionality and SHM capability of the composites [67]. Continuing with prospects of application in the aeronautics field, a 3D graphene nanoplatelets (GPN) network was developed and integrated into an epoxy matrix. These composites present a low percolation threshold of ≈1.31 vol% and exhibit relatively high sensitivity with GFs around 45. Further, the composite presents high Young's in the range of 2.2 GPa. This system proposes an effective way to detect the initiation and accumulation of damage in the composite structure when tensile stress is applied, as depicted in Figure 3 [68].

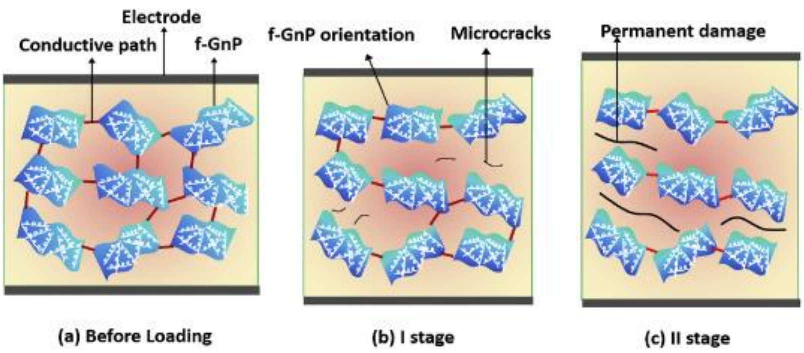

Figure 3: Schematic illustration of the damage evolution during tensile loading [68].

The concept of quantum resistive sensors (QRS) was presented as SHM possibility to detect and monitor damage without hindering the mechanical integrity of the structures. Spray layer by layer hierarchical assembly was used to fabricate the QRS based on epoxy dispersed CNTs directly on glass fibre plies surface, then connected with carbon threads and covered with several additional glass fibre layers as shown in the Figure 4. Sensors with GFs between 5 and 6 were obtained allowing a precise location by spreading them into the polymer matrix without compromising mechanical properties. This system is able to monitor an entire structure and detect changes in a specific intended zone, representing thus a potential candidate to application in aircraft wings and windmills blades for real-time monitoring of damage accumulation or even anticipation and prevention of fracture [69].

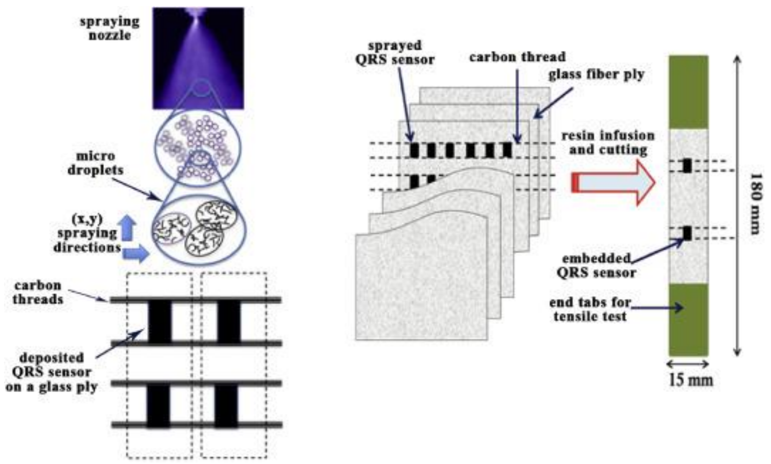

Figure 4: Schematic representation of composite samples fabrication with embedded QRS [69].

As the delamination is recognised as one of the major modes of failure in laminated composites, an interesting approach to identify this type of failure in omega stringers reinforced with piezoresistive tufted yarns was recently reported. The composite structures were produced with glass fibre reinforced with tufted carbon fibres on polyparaphenylene benzobisoxazole (PBO) yarns (Figure 5) and moulded by vacuum assisted resin transfer molding (VARTM) process. The system allied the improvement of the fracture toughness of the structure with a superior electrical conductivity, what endow the capability of measuring in real time the electric resistance variation and detect damage from the piezoresistivity [15].

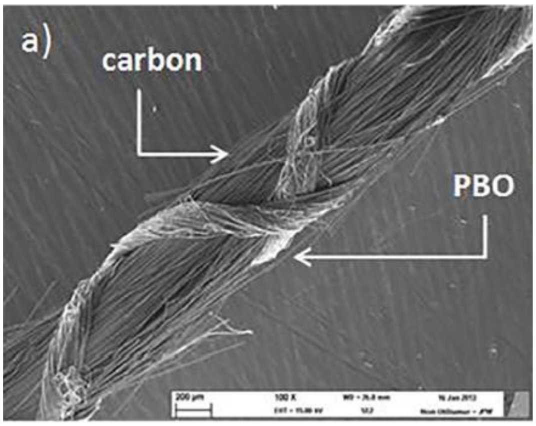

Figure 5: SEM micrograph of a carbon fibre/PBO yarn used in the tufting of a glass fibre composite with SHM capability [15].

An original approach described a multi-step developing process of a piezoresistive sensor for SHM using laser-induced nanostructure growth for the device fabrication. Firstly, ZnO nanostructures were growth onto woven carbon fibre (WCF) by continuous laser beam-assisted hydrothermal method. Then, the WCF/ZnO nanostructure was used as an electrode of a supercapacitor with a woven Kevlar fibre (WKF) as separator and polyester combined with ionic liquid and lithium slat as solid polymer electrolyte, and finally the application of the system as chargeable piezoresistive sensor (Figure 6).

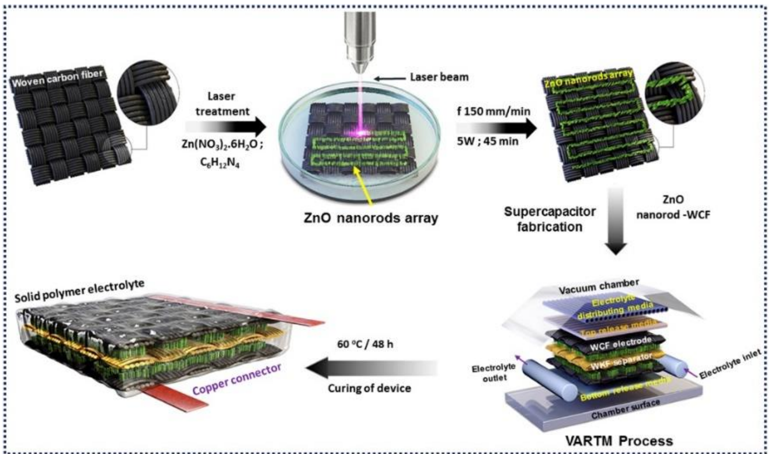

Figure 6: Schematic diagram of the ZnO nanostructures synthesis on WCF by laser beam-assisted technique and device fabrication by VARTM process [70].

The system presented an interesting sensitivity with maximum GF of 18.1 after 100 strain cycles. This innovative device was pointed as a promising useful tool for SHM of heavy duty applications, such as defect monitoring in aerospace and automobiles, crack formation in bridges and buildings, among others [70].

The comparison between different carbon allotropes as reinforce nanostructuring fillers to achieve piezoresistive SHM was subject of study employing CNTs, GNPs and conductive CB into a glass fibre matrix to obtain significant electrical conductivity. The glass fibre was functionalised with carbon nanofillers during the melt spinning process, specifically adapted for this intent, and then dispersed into a polypropylene (PP) matrix to test its piezoresistive response. Remarkable sensitivities with GFs of around 670 were registered during quasi-static 3-point bending tests [71].

In the area of biomechanical monitoring, attached sensor systems may be preferred to those embedded, namely for specific applications such as human motion detection, soft skins, smart wearable sensors and in general for monitoring systems that require integration in curved surfaces, which demand materials with high flexibility and stretchability capacities [61, 64]. The thermoplastic elastomer SEBS filled with 50 wt% of CB was proposed as a band sensor to measure strains in human body. The sensors were effective on human wrist motion capture and showed ability to identify discrete hand positions and arm rotations. The wrist mounted sensor was also sensitive to track blood pulse waves allowing to determine blood pressure during the systole and diastole. GFs between 4.3 and 6 were obtained in mechanical cycling tests and near linear signals were displayed to successively strains levels up to 50% of strain [72]. The soft elastomer PDMS filled with GNPs was studied as strain and pressure flexible piezoresistive sensor. The nanocomposite sensors showed a good piezoresistive response for strain levels about 20% and improved sensitivity for 5wt% of GNPs loadings. The sensor not only positively responded to subtle flexions but also accurately distinguished them (Figure 7), which makes these GNPs/PDMS composites promising candidates for artificial skin and wearable sensor applications [73].

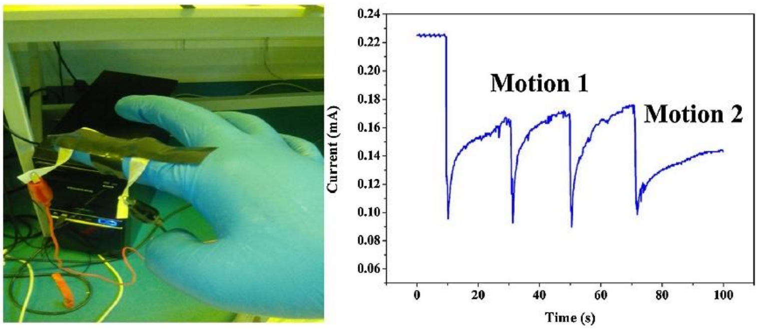

Figure 7: Piezoresistive sensor attached to a glove recording the finger movements [73].

An innovative approach presented a composite based PDMS filled with woven graphene fabric with high flexibility capable of detecting feeble human multi-mode motions, such as tensile and flexural strain, with a high piezoresistive GFs of 223 at 3% of strain. The composite sensor was integrated with Bluetooth wireless communication to create a wearable musical instrument prototype which converts human motions into music sounds of different instruments [74]. Still in the field of human health monitoring, thermal rGO doped with PS nanoparticles on PDMS substrate were used to produce a flexible piezoresistive strain sensor by laser induced reduction (Figure 8a) with GFs up to 250 for linear deformation and around 725 in nonlinear deformation. These sensors demonstrated ability in human body activities monitoring including swallowing process, lower back posture and pulse neck (Figure 8b) presenting great potential for injuries prevention or diagnosing disease-related disorders [75].

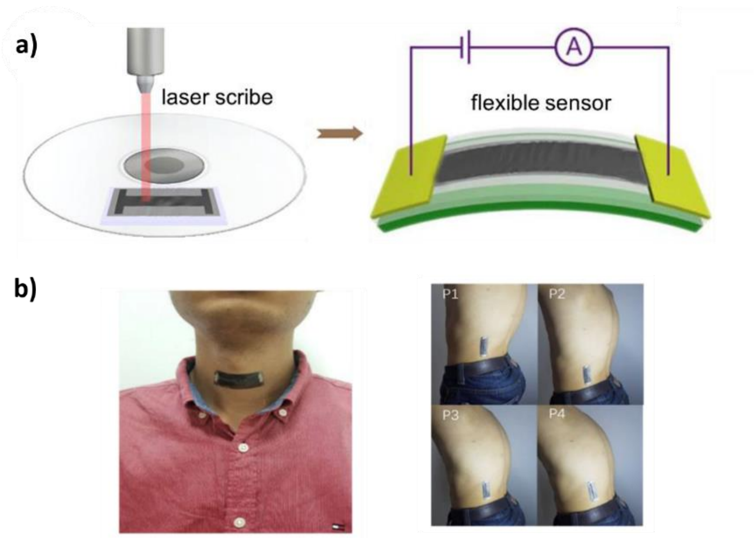

Figure 8: a) Laser scribing process of PS doped with rGO strain sensor; b) strain sensor placed for swallowing process (left) and posture human back (right) monitoring [75].

The wearable mechanical sensor technology has also been focussing increasing interest, as an example an all-flexible piezoresistive strain sensor based on graphene, microfluidic liquid metal and stretchable elastomer was developed. This sensor features encased patterned graphene inside PDMS elastomer containing microfluidic channels with liquid metal for interconnections and wiring. The system demonstrated capability to monitor strains in curved surfaces, monitor angular motions of a human wrist and multidirectional strains [76]. Similarly, skin-mountable and ultra-soft strain sensor based on CNTs and silicone rubber were presented as an epidermal electronic device able to monitor human motion for virtual reality, robotics and entertainments applications. The sensors showed high stretchability and reliability, superior temperature linearity and full recover for strains as large as 500% and exhibited electromechanical robustness for over approximately 1380% of stretching. The devices were mounted in different parts of the body (index finger, wrist and elbow) measuring the maximum strain of around 63% for elbow joint [77]. An innovative approach presented the fabrication of large area ultrathin graphene films, by an environment-friendly and cost-effective method based on Marangoni effect, for application in electronic skins, wearable sensors and health monitoring platforms. The sensors showed high transparency in the range of 86 to 94% for 550 nm and exhibited a noticeable sensitivity with a GF of 1037 at a small strain of 2% [78]. The concept of yarn sensors for tiny motion monitoring was approached through polyurethane (PU) coating, via layer by layer assembly, with a composite of natural rubber with negatively charged CB and cellulose nanocrystals. The yarn sensor showed a GF of 39 and a limit of detection of 0.1% with good reproducibility over 10000 cycles. The system was proposed for speech recognition, pulse monitoring and expression detection due to the sensitivity level [79].

Force mapping is another interesting way of SHM through attached sensors, hence piezoresistive nanographene films were proposed as strain sensors with sensitivity tuning possibilities by tailoring graphene nanostructures achieving GFs higher than 600. Moreover, these nanographene films were transferred to flexible substrates to facilitate their device integration [80]. An in-situ sensing system based on printed circuit boards (PCB) was produced by photolithography using a flexible polyimide with copper foil. The sensing mats were attached with silver-epoxy adhesive to carbon-fibre reinforced composite (CFRP) laminates (Figure 9) and showed ability to monitor strain and at the same time detect, locate and assess the damage severity on the surface and thoroughthickness of the composite panels. The change in electrical resistance of the carbon fibres were monitored by bending loads applied on a beam-type specimen. The design of sensing mats was found to be determinant for the performance, namely the distance of the sensors in the mat that showed strong influence on the electrical readings of the sensor. This system demonstrates ability to locate and size the damage on the composite structure with high accuracy level allowing thus a quick assessment to the operator, representing thus a low cost technology with possible application in the sectors of aeronautic, automobile, power generation, among others [81].

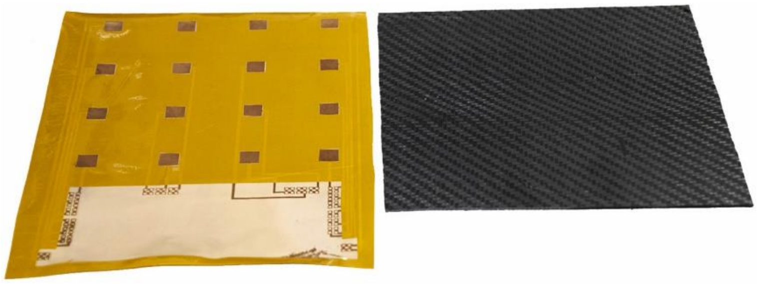

Figure 9: Flexible sensing mat (left) to be attached onto CFRP panels (right) [81].

In the same line, real-time SHM was used to detect, locate and quantify the damage in large polymer composite plates based on carbon fibre and CNT networks by mapping electrical potential variations. Epoxy resin modified with MWCNTs was used to fabricate 6 layer laminates of plain wave carbon fabric, then the plates were damage by drilling holes creation and impact loading. The changes in the electrical potential on the surroundings of the damage allows its localization. In this way, holes, impact damage and near-invisible impact damage were detected, located and quantified [82].

Some focus and effort have also been devoted in the development and optimization of piezoresistive sensors based on high stretchable and flexible materials, such as the nanocomposites of TPU filled MWCNTs with the low percolation threshold of 0.1 wt% that presented tunable strength, sensitivity and strain tolerance to work on both small and large deformation regimes. These sensors exhibited maximums GFs of 22 for 0.3 wt% MWCNT at 15% of strain, and 7935 for 1.0 wt% MWCNT at 185% of strain [19]. High stretchable conductive elastomers based on natural rubber and MWCNTs were reported as advantageous piezoresistive strain sensors due to their flexibility, ease of manufacturing and noticeable sensitivity, even with a nonlinear response [83]. Silicone rubber filled with graphene and CB presented high reversible and durable behaviour, with stretchability up to 300% [84]. PVDF nanocomposites loaded with hybrid fillers consisting of a mixture of CB and CNTs was presented as a strategy to construct a strain susceptible conductive network with tuned piezoresistive sensitivity. The nanocomposite with 0.5 wt% of CB and CNTs presented the highest $\Delta R/R_0$ of 0.65 at 10% of tensile strain, which is higher than that registered for CNTs networks [85]. Exploring a comparative view, flexible PDMS composites were prepared alternately with 0.48 vol% of CB and with 0.13 vol% of CNTs. Both sensors showed linear behaviour and reproducibility with GF of 15.75 for CB and 4.36 for CNTs, at 10% of strain. PDMS/CB composite proved to be more stable in long-term cyclic tests. Further, a mathematical model was proposed to explain the two distinct mechanisms and smart gloves detecting finger motion were assembled using the fabricated sensors (Figure 10) [86].

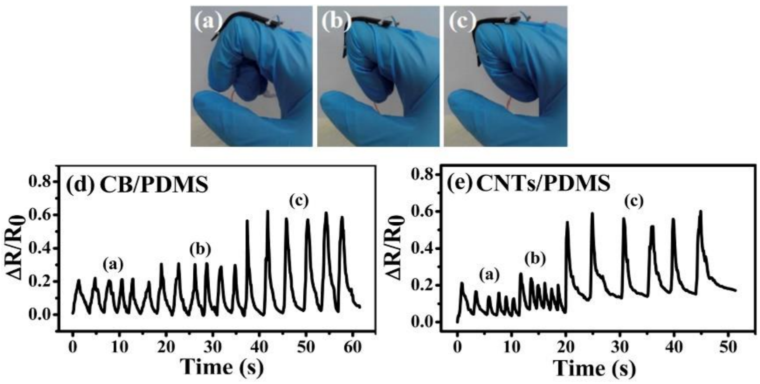

Figure 10: Smart glove assembled with strain sensors at different bending angles (top); sensing behaviours of the PDMS composites on glove motion detection (bottom) [86].

Ternary composites composed by olefin block copolymer (OCB), TPU and CB, produced by extrusion process, were studied for application as small and large strain sensors. The ratio of 50:50 between TPU and OBC was kept constant for all composites and the content of CB varied. These ternary systems showed promising results for both low and high strain ranges in cycling testing, achieving the maximum GF of 64 at low strain range between 0 and 3% for 10 wt% of CB, and the GF of 4.2×10^4 at high strain of 85% for 12 wt% of CB [87]. The high sensitivities allied to the well-stablish and ease scale-up industrial production process makes these ternary composites promising candidate for force and deformation sensing applications [87].

In short, functional materials for SHM and biomechanical systems can be divided into embedded and attached, presenting the corresponding advantages and drawbacks depending on the type of application. The piezoresistive embedded sensors are more adequate to monitor and prevent different modes of damages on large structures, taking advantage of the electrical properties of the functional structures in a self-sensing operation mode, without sacrificing structural properties and benefiting of the high accuracy and reliability of this type of sensors. The attached sensors are more directed to human healthcare monitoring or wearable sensor devices, in particular when curved surfaces monitoring is required, since this type of systems present larger versatility and open a wide range of integration possibilities.

5. Printable applications of piezoresistive composites

5.1. Solvent based inks

Research in piezoresistive sensing elements includes aspects such as the development of suitable materials, manufacturing techniques, and system integration strategies [15, 62]. Applications related to piezoresistive sensing materials include mechanical and aerospace structures [62] and may require the use of sensing devices that can be patterned or deposited onto shaped and complex morphologies. To meet these requirements, the combination of stretchable materials and printing technologies can be a suitable approach to direct fabrication of patterned devices [88, 89]. This combination can offering an increase in precision and effectiveness of sensor integration, which is essential for optimizing the potential applications [89].

Piezoresistive sensors are particularly interesting in aeronautic components [90], such as aircrafts who are exposed to different environmental effects (temperature or impact by birds, for example) that can affect their structural integrity. Thus, strain sensors based on ternary composites with good performance in monitoring cracks in aerostat surfaces was reported [90]. The composite is based on polydimethylsiloxane (PDMS), carbon black (CB), and carbon nanotubes (CNT) and fabricated by screen-printing and transfer printing techniques. The piezoresistive sensor exhibited remarkable durability (over 10^5 cycles at 25% strain), high sensitivity (GF ≈12), good linearity and reproducibility. Figure 11a shows the monitoring of crack progression, which is detected as an increase of electrical resistance until the structure totally fractures. A flow sensor was also fabricated based on a conductive composite elastomer that acts as piezoresistor [91]. This type of sensors are suitable for flight control systems, including detection of airflow separation on the leading edge of aircraft wings, and in situations where high flight speeds/extreme maneuvers are required. Device fabrication involved multiple processing steps and materials, using printing and laser micromachining techniques. In particular, a CB/silicone-based elastomer composite was patterned on a microtuft (Figure 11b). When this microtuft is exposed to the flow, strains are induced due to a drag-torque displacement mechanism, and the strain eventually changes the resistance of the piezoresistor as a function of the applied airflow. This fabricated sensor can be mounted on curved surfaces.

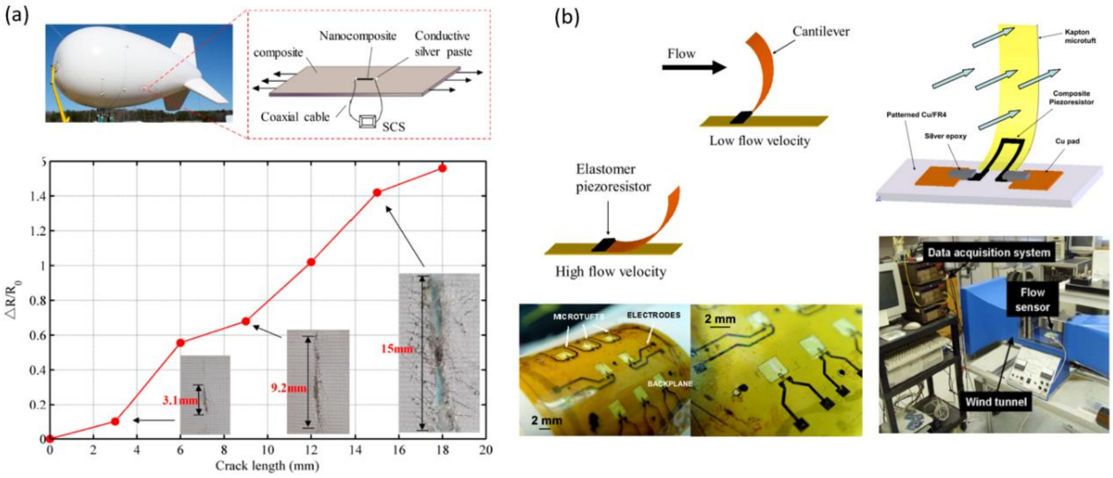

Figure 11: Examples of printed piezoresistive sensors. (a) Crack detection of aerostats, and resistance change ratio of the strain sensor under crack propagation. (b) Schematic representation of flow sensors, flexible sensor array, and wind tunnel testing setup with data acquisition system [91].

Another important application of printable piezoresistive sensors is in civil engineering structures, including bridges or buildings, among other structures. For instance, Figure 12 depicts a printed strain sensor arrays built for detecting and localize cracks in a bridge structure [92]. These sensors were fabricated by screen-printing of a thermosetting graphite ink over a copper/polyethylene naphthalate (PEN) laminate. Because of the temperature sensitivity of the graphite ink, it was implemented a full-Wheatstone-bridge sensor that provides reliable strain measurements over a wide temperature range, which is required for its practical use. In addition, stretchable strain sensor devices can also be developed for structural monitoring of concrete structures [93]. The flexible CNT/PDMS composite sensor was fabricated via solution casting method in order to monitor the deformation, first-crack strength, and detecting compressive strain. Figure 12b shows the stress/resistance change of the composite as a function of deflection. It is observed that the resistance of the composite increases rapidly in the BC stage after a visible crack occurred. This macroscopic crack was found at point B in the bottom surface of reactive powder concrete. In addition, sensitivity results show significant change in electrical resistance when subject to large tensile strains, and repeatable resistance change in response to cyclic loadings of mechanical strain.

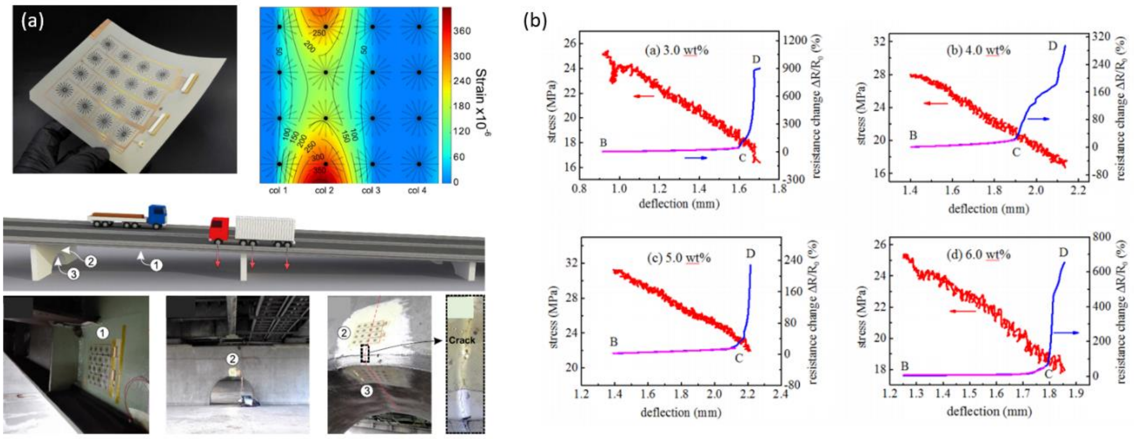

Figure 12: Examples of piezoresistive sensors used for civil engineering applications. (a) Fabricated array of 16 strain sensors, mapping of strain distribution, and location of sensor arrays attached to a bridge [92]. (b) Resistance change of MWCNT/PDMS composites versus deflection of reactive powder concrete under three point bending test [93].

Many research efforts have been devoted to the development of new functional inks and processing strategies. For example, a metal-metal composite based strain sensor has been developed by screen-printing of a silver nanowire/silver flake ink on a flexible and stretchable thermoplastic polyurethane (TPU) substrate [94]. These metal-metal composites are a promising solution for applications in civil infrastructures as in a wavy line strain sensor configuration, the sensors show a 33% change in resistance for every 1% of strain. Further, strain sensors based on poly(vinylidene fluoride) (PVDF) reinforced with carbonaceous nanofillers have been developed by melt mixing using a micro compounder [85]. The effect of different fillers contents on the electrical conductivity and piezoresistive sensitivity of the composite was evaluated. The highest strain sensitivity with a $\Delta R/R_0$ value of 0.65 at 10% strain was obtained for the composite with 0.5 wt% CNT and 0.5 wt% CB [85]. This composite combines both relatively wide strain sensing range as well as a high sensitivity.

Thus, printing technologies as suitable for the development of piezoresistive composites and their integration into force and deformation sensing applications, as well as in SHM applications. In particular, the possibility of replacing rigid substrates, capability to achieve predefined complex shapes, and direct generation of sensing patterns are among the largest advantages. However, further progress is required based on novel designs, new printable functional composites, and new integration strategies to increase the functionality of the printed sensors devices.

5.2. Fused Deposit Modelling

There are different 3D printing processes allowing to obtain structural parts from a wide variety of polymeric soft materials [95-97]. Each printing process requires the material in an adequate disposition, appearance (resin, filament, pellets or powder) and good technical structural condition (diameter, distribution of sizes, viscosity), thermal and adhesion properties [95-97].

Laser curing [95, 98] and light [95] printing processes usually just deal with one type of material. However, the systems of Fused Deposit Modelling, FDM, feeding the material in the form of solid filaments, is the most extended method for 3D printing [95] and allows a direct use of various materials, using several fusion extruders [97]. This allows to gather materials with distinct functionalities during the construction of a 3D piece according to the design requirements.

FDM printers with two and three extruders allow printing parts with different polymers and colours, allowing to fabricate different support materials and to combine rigid to flexible substrates. Further, these techniques also allow to develop electronic devices by 3D printing, using different polymers with novel and interesting mechanic and electrical properties. As an example, printers allow to print insulating polymers combined with electrically conductive materials and sensing materials, all printed in a single printing process. It is also possible to associate several types of extruders with other processes, such as conductive paste disposal systems or laser treatment, to develop hybrid processes.

5.2.1. Fused Deposition Modelling Process

The 3D printing technology from polymeric thermoplastics in the form of filaments receives different names but Fused Deposition Modelling, FDM, is the most used nomenclature. FDM consists in feeding by dragging with a traction motor and fusion of a polymeric filament through a hot extruder nozzle. The 3D part is defined at the surface level and is distributed in layers of defined thickness and area. The process is completed by successively superimposing layers and building the piece in a layer by layer process. From linear to complex geometries, 3D printed structures is revolutionizing the fabrication of prototypes and structure.

5.2.2. Materials for FDM

The first and most common material for FDM was polylactic acid (PLA) [99] and its bioderivatives [100], followed by the copolymer acrylonitrile butadiene styrene (ABS) [101]. Different technical polymers such us polyamide (PA) or polycarbonate (PC) and elastomeric polymers such us thermoplastic polyurethane (TPU) [88, 102] are also available, as well as polypropylene (PP) and styrene-(ethylene-butylene)-styrene (SEBS) block copolymers SEBS/PP [103], and elastomer ethylene vinyl acetate (EVA) [104], among others.

In the case of highly elastic materials, the drive system by means of the motor pushes the filament into the melting barrel and if there is too much friction it can cause a buckling effect, resulting in improper feeding of the material. When the filament feeding system is a Bowden type instead of direct feeding, this problem is further increased and can result impossible to print. In this case, the systems of direct feeding from the extruder in the form of pellets is more appropriate and the process is called fused layer modelling (FLM) [104].

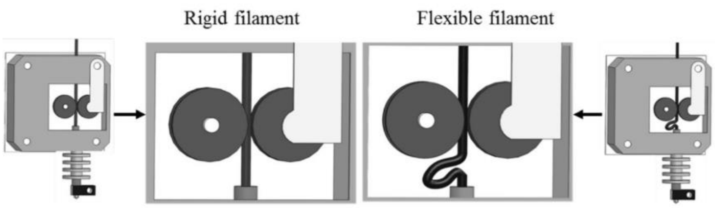

Figure 13: Buckling occurring with the feeding of the highly flexible filaments [9].

The commercial possibilities for FDM printing are wide and competitive with respect to filament materials. There are two standardized filament diameters for FDM printing equipments: 1.75 and 2.75 mm in diameter, being very important to ensure the circular section of the filament and a regular thickness along its length to provide adequate feeding and arrangement in the extruder head.

5.3. Conductive and Piezoresistive Materials for Fused Deposition Modelling

Tailoring the polymers with reinforcing conductive materials is mandatory to be able to print piezoresistive or conductive materials by 3D printing. The first step in this direction were achieved in the last decade where the overall properties of the polymer and corresponding composites were investigated and optimized [29, 41, 61]. Extruding polymer-based materials with appropriate geometry and physico-chemical properties allows to develop novel materials to be used in 3D printing processes. Together with the developments in the academic area, there are nowadays commercially available conductive filaments for FDM printing. Carbon nanoparticles or metallic nanofilaments are reinforcement materials typically used in polylactic acid (PLA) polymer for developing conductive filaments [88, 97], but piezoresistive composites filaments for multifunctional structural parts are practically non-existent in the market.

Accurate measurements of the electrical resistance of the specimens is essential and is determined by the nature of the material to be printed and the length/section ratio of the printed track [97].

In order to determine the piezoresistive properties, the changes in the electrical resistance are due to the common changes in the intrinsic and extrinsic contributions to the piezoresistive response, but also to variations in the printed material due to the changes in orientation of the nanofillers brought by the printing process [88] when submitted to external mechanical solicitations.

5.3.1. Printed Strain and Force sensors

One of the first piezoresistive materials printed by FDM was developed around 2012 with the idea of generating flexible sensors [105], based on PLA and carbon black as conductive reinforcement [105]. PLA was printed in fingers shape to overlap a silicone glove, allowing hand manoeuvrability. The composite piezoresistive sensor material was placed in a strip on each finger to record its deformation [105].

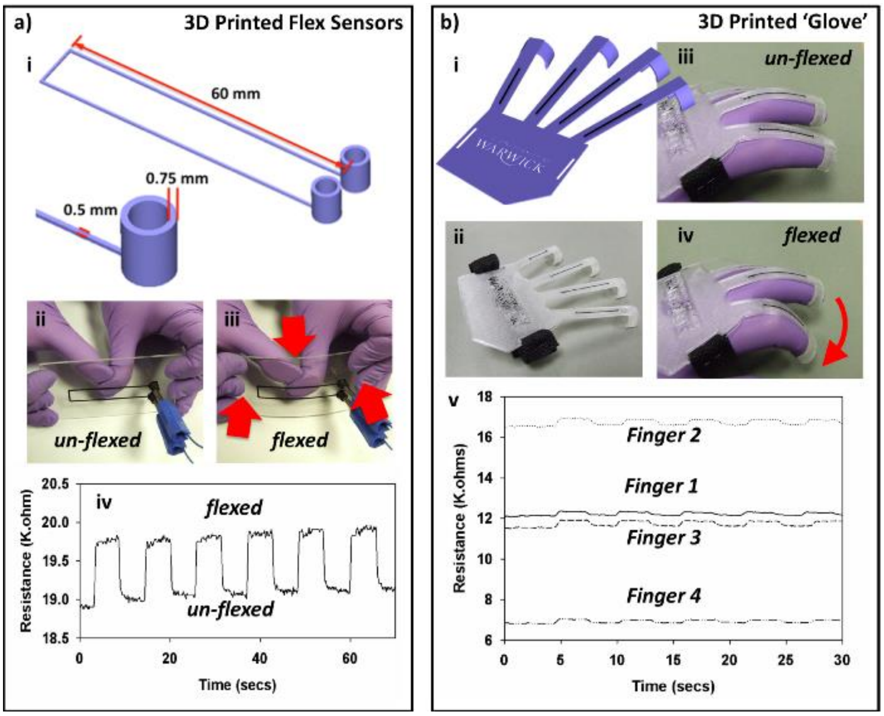

Figure 14: 3D printed 'glove' for flexing movements determination based on resistance response variation with the movement of the fingers [11].

A related application using highly conductive and flexible 2D circuits was based on PLA filled with a 6 wt% (weight percentage) of graphene [106], the 3D printed PLA composite under mechanical deformation (bending or stretching) changing proportionally the electrical resistance [106].

The multifunctionality of these types of composite materials have been reported as a multiaxial force sensor that can measure the forces in three orthogonal axes [102]. A 3D cubic cross structure was fabricated with two different components, commercial TPU filament for the structural part and a functionalized nanocomposite filament composed by conductive carbon nanotube (CNT) reinforced TPU material as the sensing material . The sensing part (Figure 15) allows to monitor the mechanical inputs to the structural component as a electrical resistance variation [102].

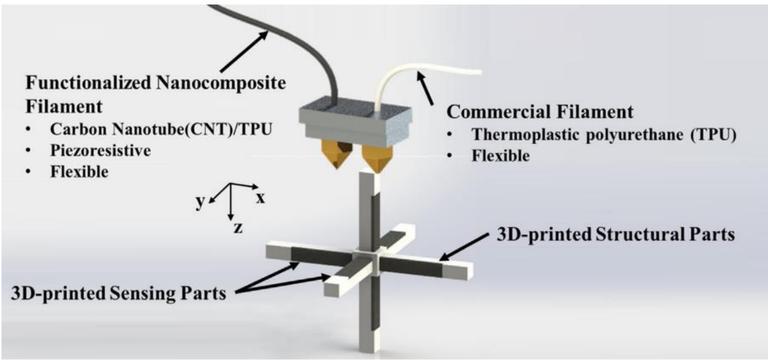

Figure 15: Schematic design of a 3D-printed multiaxial force sensor and its fabrication principle based on FDM type 3D printing [102].

TPU is a widely used polymer for 3D printing that has been used for the development of CNT reinforces composites working as piezoresistive sensors [88], showing excellent cyclic piezoresistive performance with gauge factor as high as 176 [88]. Thus, TPU composites allow high performance 3D printed deformation sensors [88, 96], that can be manufactured using additive manufacturing techniques such as FDM.

The 3D printed sensors demonstrate excellent mechanical properties and piezoresistive performance with high gauge factor (GF larger than 150) [88, 96], large strain range (larger than 200%) [88, 96], good stability (up to 1000 loading/unloading cycles) and wide frequency response range of 0.01–1 Hz [102]. Those sensors have been implemented to monitor human body movements (finger movement, wrist bending, and breathing) and voice, showing its potential for applications in intelligent robots and wearable electronics [89, 95, 96, 102].

5.3.2. Embedded sensing: wearable sensors in 3-D printed structures

A novel and stimulating approach is to combine different manufacturing processes such as printing functional materials using FDM and adding the conductive circuit or other electronic component through other printing processes such as micro-dispensing, Aerosol Jet^{TM}, or Direct Print Photopolymerization (DPP) process [107]. Other approaches combine structural and elastics materials printed by FDM with conductive materials printed by micro-extruders for printed electronics and embedded sensing materials [108]. In those cases it is particularly relevant to finish the surface of the material printed by FDM to ensure a good adhesion between both printed materials [98, 109].

Conclusions

The current technology developments in 3D printing and the research in polymer-based composite materials with advanced and multifunctional properties enable to develop new sensor materials for Industry 4.0 and Internet of Things (IoT). This approach allows to revolutionize the way devices are fabricated and implemented (complete devices or part of them), allowing to introduce tailored mechanical, electrical and functional properties of materials in 3D printed specific structures and/or structural parts.

Thermoplastic and elastomer polymers with functional properties are increasingly being applied as sensors materials and directly implemented in the structure and not just as external devices.

Piezoresistive and conductive materials developed from polymeric materials allow increasing the number and implementation areas of sensor devices with strong increase in Structural Health Monitoring and biomechanical devices. From flow to crack sensor, printing technologies allows, in a low-cost and greener way, innovative structural monitorization.

In a near future, this kind of materials will be implemented in commercial applications in areas ranging from automobiles, aircrafts or civil structures, to wearables and sport and biomedical devices, allowing a self-sensing and interconnected future. Highly stretchable sensor materials are also a key issue in applications involving large deformation sensor with accurate performance. Lightweight polymer-based materials will play an essential role in this type of sensors as well as printing technologies, allowing simple integration and environmental friendlier applications.

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