Chapter 3

SHAPE-MEMORY NANOCOMPOSITES FOR MULTI-RESPONSIVE POLYMER MATERIALS

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ABSTRACT

Shape-memory polymers (SMPs) are currently a subject of tremendous attention from both - the academic and industrial fields and are playing a major role in inspiring the design of a class of polymer materials. Their attractive properties related to multi-step shape-changing upon exposure to an appropriate stimulus, as well as high elastic deformation, low density, relatively low cost, ease of processing, chemical stability and biocompatibility make SMPs suitable for numerous real world applications. As if that's not enough, fabricating nanocomposites *via* the incorporation of nanofillers offers the possible applications as innovative materials with designed functionalities and multi-responsiveness even further. Nowadays, these polymer materials can be used as biomedical devices (implants, sutures, stents, drug delivery systems), actuator systems, sensors or deployable hinges for automotive, electronics and aerospace industries. In this chapter, a short description on SMPs chemical architecture, nanofillers incorporation and approaches for 3D printing are outlined. The content would also mention some potential application of the printed parts and final critical remarks.

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Keywords: shape-memory polymer, shape-memory composite, nanofiller, smart materials, 3D-printing

INTRODUCTION

1. General Overview

1.1. Historical Prologue

The study of the technological development of humanity has been a subject of passionate discussion, leading to the definition of different stages - from most primitive to present day. This vision was proposed by a Danish archaeologist named Christian Jürgensen Thomsen (1788-1865) who suggested that no one would have used stone tools once their bronze equivalent had been produced. Respectively, nobody would have used the bronze tools while iron tools were available. Today, there is little doubt that, the use and discovery of new materials has been a major factor in the development of human civilization. Traditional structural materials like wood, glass, steel, iron, and others, are still plentifully used. Slowly yet steadily, over the years new functional materials have appeared to replace them. As one of those newcomers, synthetic materials were developed by the relatively young plastic industry, but in 1989 the manufacturing of plastics managed to finally surpass even steel production [1] giving the birth of the current "Smart Materials" age [2] (Figure 1).

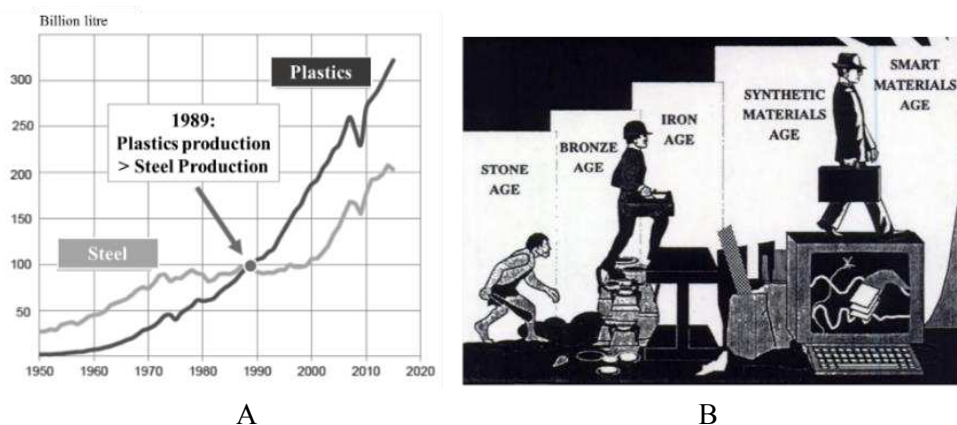
A   B

Figure 1. Volumetric comparison between steel and plastics production between 1950 and 2015 [Plastics Europe Market Research group] [1] (A) and caricature of the Human evolution relative to the materials growth [2] (B).

1.2. Shape-Memory Materials

Shape-memory materials (SMMs) are a new class of smart materials including shape-memory alloys (SMAs), polymers (SMPs), hybrids (SMHs), ceramics (SMCs) and gels (SMGs) (Figure 2). They carry a very interesting main characteristic - they can memorize a second (temporary) shape in addition of their original shape, while still being able to revert to the state of origin exposed to an appropriate stimulus.

This behavior - called a shape-memory effect (SME) was mentioned for the first time in a patent from Vernon in 1941. The invention relied upon the "elastic memory" of a synthetic resin and the listed application was molding of dental objects [4]. Later in the 1960s, cross-linked polyethylene with new shrinking properties was a subject of another patent by Rainier [5].

This work gave the possibility to produce at industrial level heat shrinkage tubing and films, later successfully commercialized without being actually recognized as SMPs. In the late 1980s, the CDF Chimie Company (France) developed the polynorbornene-based SMPs, followed by another significant scientific effort only 10 years after - the discovery of polyurethane-based SMPs by Mistubishi Heavy Industries Ltd.
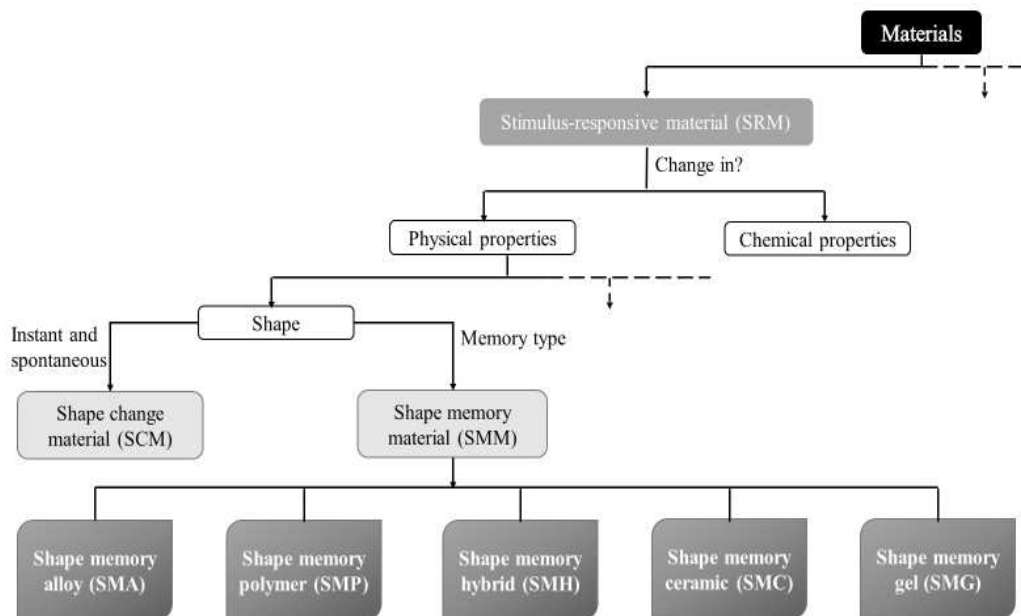

Figure 2. Classification of different SMMs [3].

1.3. Shape-Memory Polymers and Nanocomposites

In this historical context, out of the different SMM classes, SMPs have enjoyed a remarkable interest from both scientific and industrial community, and are consistently studied in the literature as evidenced by an increasing number of publications over the last twenty-five years [6-10] (Figure 3). A very likely reason for this focused interest are

the multitude of interesting qualities those materials possess - a low density, relatively low cost, high potential of recyclability and processing, transparence, high recoverable strain within a wide range of stimuli, chemical stability and modification, biocompatibility and various degradation rate of biodegradability [3]. Remarkably, SMPs can even be programmed for (multi)stimuli-responsiveness and recover their initial shape upon direct or Joule heating, heating from radiation and laser source heating, microwaves [11, 12], pressure-responsive [13], moisture, solvent or solvent vapors [14], as well as change in the pH values [15]. With all those advantages, however, come several severe limitations - a low tensile strength and stiffness, stimuli-responsive actuation restricted mostly to heat-related treatment and an absence of proper function. We could also add to the list relatively low thermal conductivity, low stiffness and high SME inertness to external stimuli (light and electro-magnetic) during actuation procedures.

One promising strategy to overcome these difficulties is the incorporation of one or more (in)organic nanofillers (nanotubes, nanofibers, nanospheres, nanorods, etc.) within the SMPs polymer matrix, thus giving origin to the shape-memory nanocomposites (SMNCs) [16, 17]. Due to their high specific surface area, high stiffness and inherent functionalities (electrical conductivities, water-responsive, etc.) the nanofillers play the role of reinforcement agents leading to an all around improvement of the physico-mechanical, thermal, mechanical and electrical properties of the materials [18]. Subsequently, it is possible to confer to the materials the desired multi-stimuli-responsiveness and functionalities enlarging the field of their potential application as smart textiles [19], medical [20] and flexible electronic devices [21], sensor and actuators [22], high performance water-vapor permeability membranes [23], self-deployable structures [24, 25], filaments for 3D printing [26] and many others. As of late, SMNCs have gained already attention in the production of innovative polymer materials as confirmed by the number of published scientific articles (Figure 3).
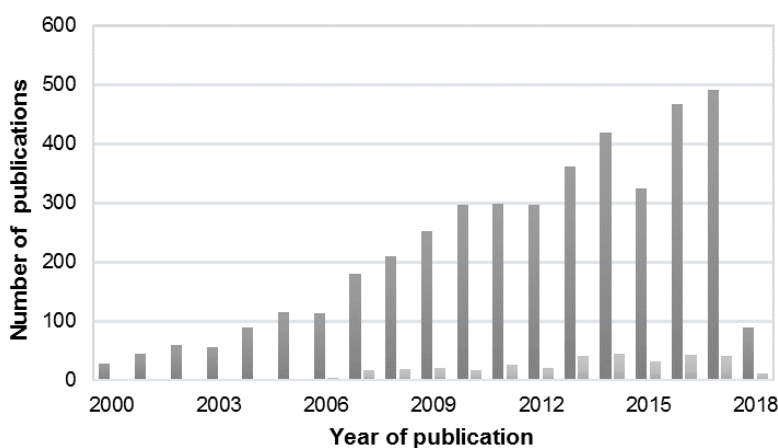

Figure 3. Number of scientific publications per year on the SMPs (darkest bars) and SMNCs (brighter bars). The data research was made on Scopus®, Elsevier B.V. on February 2018.

In the frame of this chapter, a brief review of the SMPs chemical architecture and recent trends in the field is presented with particular focus on SMNCs their structure, shape-memory effects and working mechanism.

2. SMPs for Multi-Responsive Materials

2.1. Definitions and Generalities

Accepted by the scientific community, SMPs are described as polymers capable to memorize a permanent shape, to acquire a temporary one upon deformation during the programming step and to revert back to their original shape when an appropriate stimulus is applied during the recovery step (Figure 4). The capacity of the polymer for recovery from a fixed shape to the initial one is defined as the SME [27]. This effect can be reversible upon subsequent programming process and quantified by the fixity ratio (R_f) or the capacity of the polymer to fix the temporary shape and the recovery ratio (R_r) related to its possibility to reach the original shape [28].
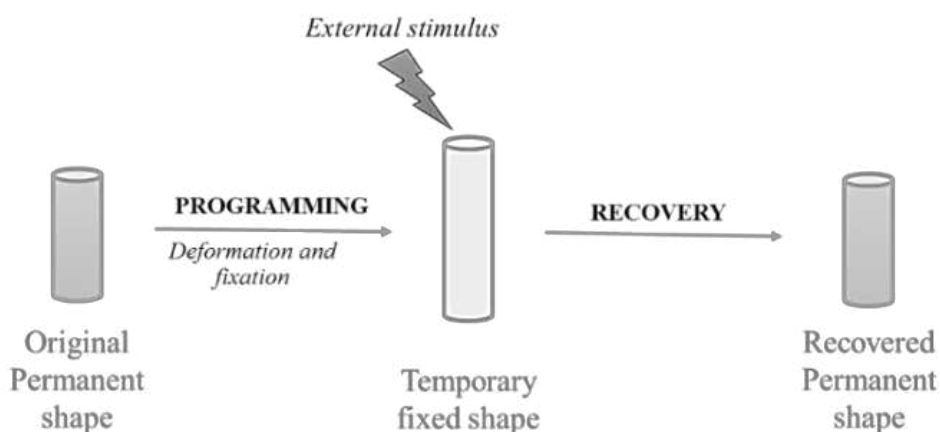

Figure 4. Schematic illustration of SME.

The SME is not an intrinsic property of the polymers but rather results from the combination between a particular polymer morphology (switching and permanent domains) and a stimulus program. To elaborate, a key element is the predefined arrangement between the polymer structure/morphology and the applied programming process [29]. In general, the SMP chemical architecture results in the coexistence of a permanent and a switching domain: the former is made of chemical or physical cross-links [interpenetrated network (IPN) [30-32] or interlocked cyclodextrin supramolecular complex [33-35]] and the latter of stimuli sensitive fragments (crystallization/melting transition, vitrification/glass transition or liquid crystal anisotropic/isotropic transition in

the case of heating-responsive SMPs) [36] (Figure 3). The fixation of the temporary shape and the shape recovery to the initial one results in so-called controlled reversible triggered switches (reversible molecule cross-linking and a supramolecular association/dissociation). In all types of actuations, the entropic elasticity of the polymer network is a driving force for the shape recovery process [37].
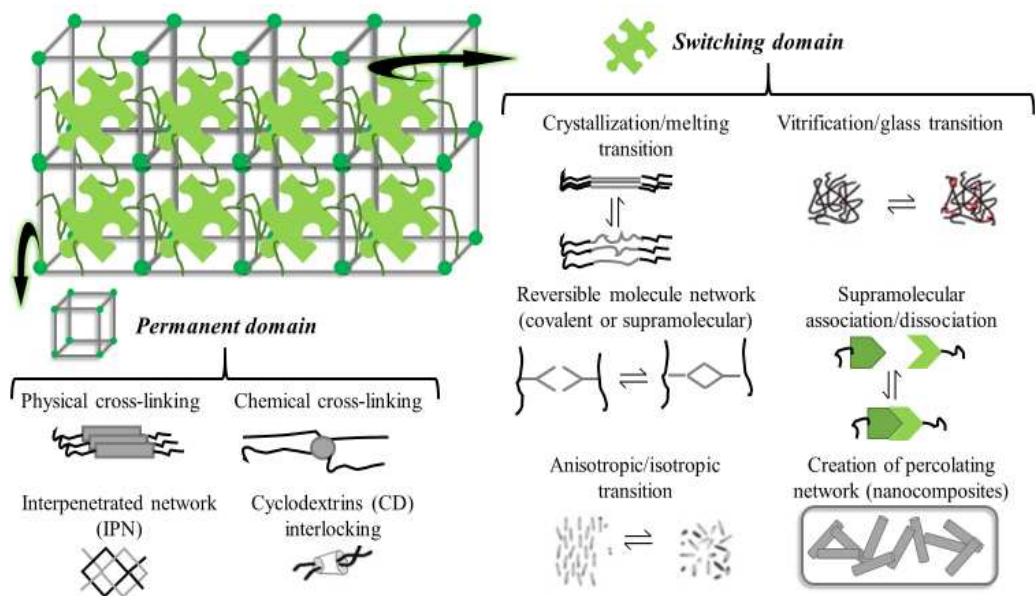

Figure 5. General presentation of SMP chemical architecture and permanent and switching domain building blocks concept.

Most of the SMPs systems are characterized with "one-way" (1W-SME) heating-triggered response in relation to their thermal transitions [glass transition temperature (T_g) and melting temperature (T_m)]. "Two- (2W-SME) and multi-way" polymers are the subject of several studies for their ability to change reversibly their shape with multi-stimuli responsiveness, thus offering an even greater to design polymer actuators [38]. This could be of interest for artificial muscles fabrication as well as devices with multiple degree of freedom for endoscopic surgery application and obtained from: cross-linked semi-crystalline polymers [39-42], nematic liquid-crystalline elastomers [43, 44], and glass-forming polydomain nematic networks [45]. Usually, the actuation phenomenon occurs during the heating and cooling step by reversible chain conformations in presence or absence of external stress. Polymer devices with actuator behavior were described by Chung et al. for poly(cyclooctene) (PCO) films covalently cross-linked by dicumyl peroxide [42].

2.2. Polymeric Actuators

Previously, it was reported that the "2W-SME" of the semi-crystalline thermosets can be easily controlled by adjusting the degree of the polymer matrix cross-linking [46]. Using a working temperature close to the material T_m it was possible to increase the strain during the cooling step revealing the reversible shape effect. In addition, when the sample was heated upon constant stress, a tensile contraction of the PCO appeared responsible for the shape recovery similar to the one observed before crystallization. More complex systems based on crystallization induced elongation and melting induced contraction phenomena were described for multiphase polymer networks [star-precursors of polypentadecalactone (PPDL) and PCL] [47] (Figure 6). Potentially interesting, thermo-reversible cross-linked PCL-based PU networks with pronounced "2W-SME" were reported by Raquez et al. in 2011 using reactive extrusion as technology of choice [48]. The main advantage of the used Diels-Alder cycloaddition reactions (between furan and maleimide moieties), was the easy control of the microstructure and the cross-linking density by partially replacing PCL-diol with PCL-tetraol. This SME can be also obtained without applying a constant stress as in the case of a multiphasic copoly(ester-urethane) network made of, at least, two semi-crystalline polyester segments (PCL and PPDL) [49]. Another strategy is to form an internal skeleton based on crystallites huddled in nano-clusters playing the role of physical network and adjusting the degree of actuation of the domains [50]. For this purpose, cross-linked poly[ethylene-*co*-(vinyl acetate)] (cPEVA), with a broad T_m (in the range from 25°C to 90°C), allowed the formation of two types of polyethylene (PE) crystallites. By taking advantage of the presence of two T_m it was possible to actuate step by step the device: lower T_m defined as the actuation domain (from $T_{m,onset}$ to intermediate T_m) and the other thermal transition was activated by the upper range (from the intermediate T_m to $T_{m,offset}$). As a result, the main network was create after applying a certain stress directly after the cooling step ($T_{m,onset}$, 25°C). Another strategy is the design of IPN combining the crystalline component of PCL (switching domain) and the elastomer poly(tetramethylene ether)glycol (PTMEG) acting as a spring [51]. In this case Pre-IPN was first obtained by previously dissolving macromonomers and cross-linkers in dimethylformamide, leading to the production of photo-crosslinked of acrylate-PCL. Stretching the resulted gel-like structure and the subsequent curing/cooling step of the PTMEG at 80°C allowed the formation of the elastomeric network.

The reheating of the sample allowed the PCL to melt by "opening of the switch." Then the PTMEG underwent a compression movement and the polyester segment can crystallize upon cooling following the "spring direction." With this example, the authors demonstrated the possibility to build tension-free 2W-SMP systems for artificial muscles or tendon application (Figure 7).
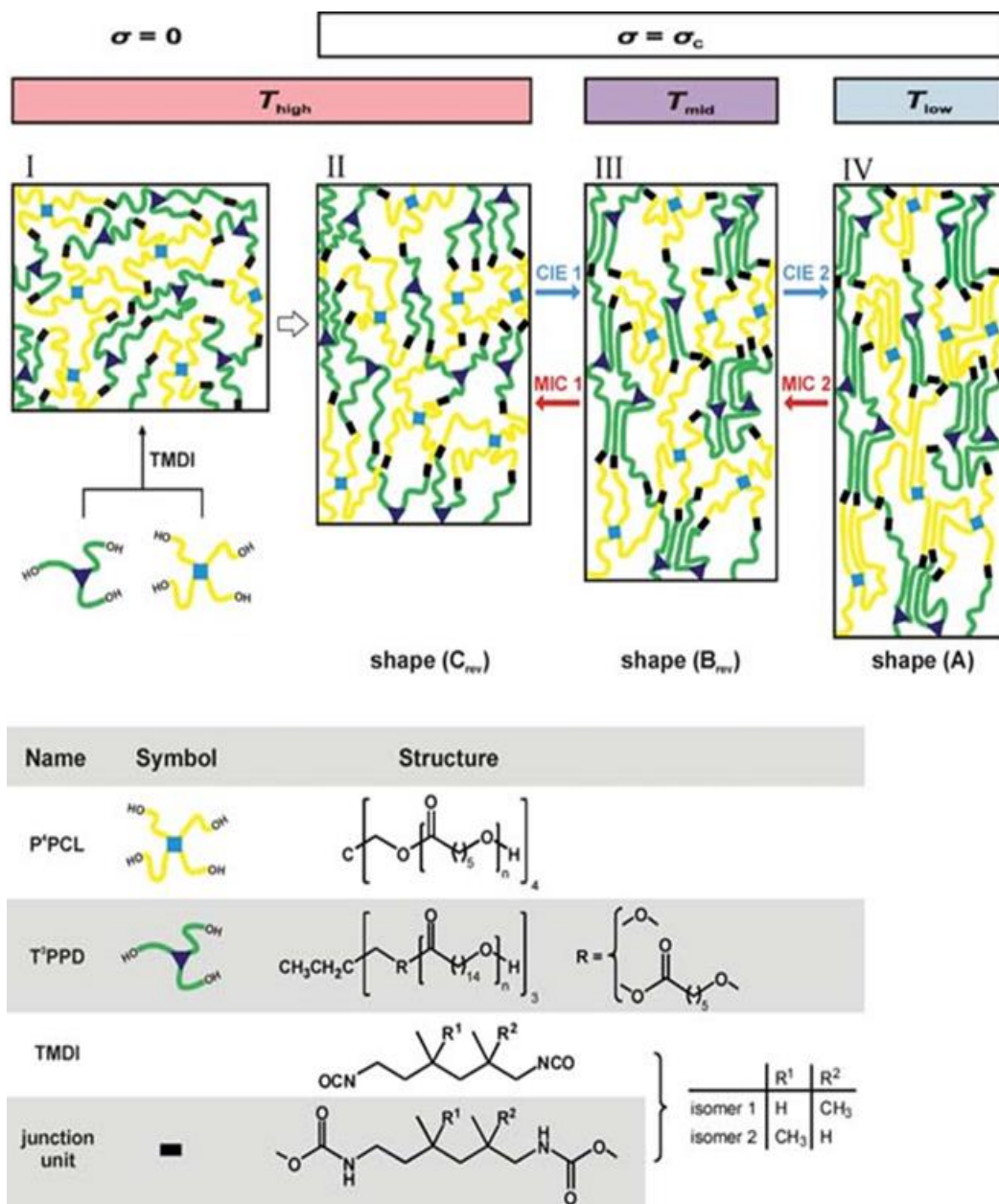
Figure 6. Reversible t-SME in PCL- and PPDL-based network [47].

For more clarity the SMP "1W-, 2W- and multi-way SME" mechanism are not discussed in detail in the present chapter. The readers are kindly invited to consult the available data on the topic.
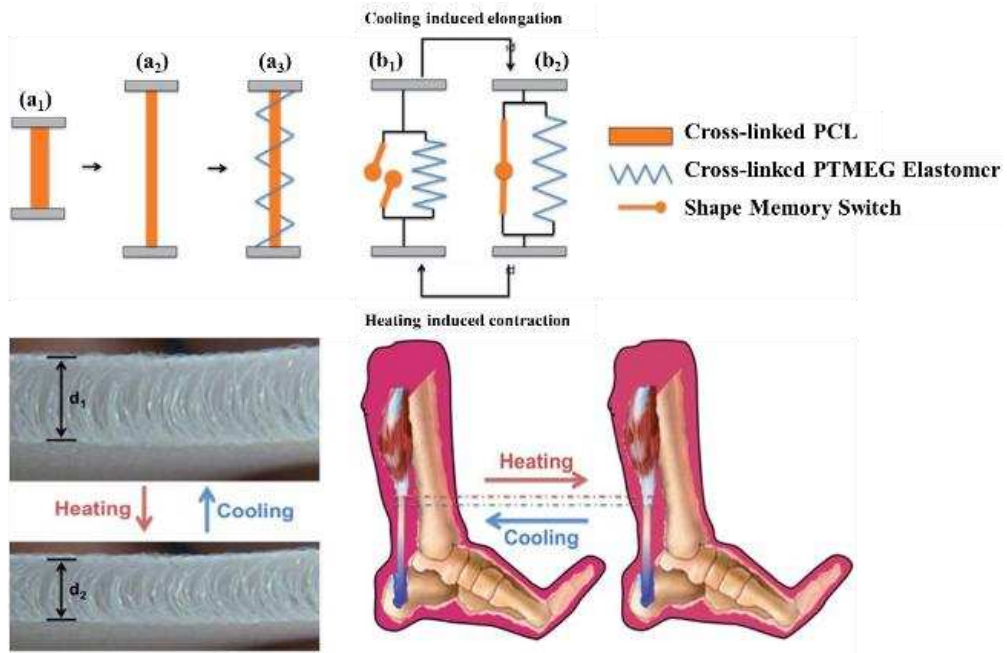
Figure 7. "2W-SME switch spring" actuated system for artificial muscles or tendon application; a_1 - cross-linked PCL, a_2 - stretched fixed PCL, a_3 - cross-linked PTMEG, b_1 - compressed shape, b_2 - elongated shape [51].

3. Multi-Responsive SMNCs

In the previous section, one of the more common and convenient way to actuate the SMP materials was described - direct sample heating or increasing the environmental temperature. However, this is not really suitable for all applications. An elegant strategy to increase the sample temperature is to incorporate functional nanofillers into the SMP matrix. In this way it will be possible to convert various energy (electrical, magnetic, optical, acoustic or chemical) to heat and to act on the thermal transitions of polymer devices. In the following section, the possibility to produce temperature- or magnetic field-memory, as well as water-sensitive SMPs is outlined and some of the potential applications are pointed out.

3.1. SMNCs Containing Carbon-Based Nanofillers

Up to date, one of the most studied SMPs materials are the electrically conductive polymeric nanocomposites. They can be easily obtained by the incorporation of nanofillers capable to convert the electrical current into heat through Joule effect such as: single-walled carbon nanotubes (SWCNTs), multi-wall carbon nanotubes (MWCNTs), carbon nanofibers (CNFs), carbon nanopaper, aligned conductive carbon-based nanofillers, carbon black (CB) and graphene.

Carbon nanotubes is the most promising reinforcement materials, capable of carrying a current density as high as 1×10^9 amp/cm^2 [52] while showing good flexibility compared to conventional fibers [53]. The good overall performance of electrically conductive SMNCs is directly related to the dispersion of the nanofillers in the polymer matrix, the interaction with the polymer chains and the establishing of the percolation network. In return, this affects the materials' final mechanical and thermal properties and restricts their potential applications. In order to overcome said difficulties, several strategies have been developed: (*i*) direct blending of the (MW)CNTs with the polymer, (*ii*) (MW)CNTs surface-modification (improvement of the interfacial interactions with the polymer macromolecules), (*iii*) cross-linking the (MW)CNTs with the polymer matrix, (*iv*) alignment of the (MW)CNTs in the polymer material or (*v*) conversion of the (MW)CNTs into nanopaper or film and its incorporation within the polymer system [54].

In most cases, the direct (MW)CNTs blending approach with the polymer matrix cannot avoid entirely the formation of nanofiller aggregates (lack of functional sites on the conductive nanofillers surface capable to interact with the polymer matrix). A good workaround is to prepare films and yarns, as paper-like (MW)CNTs films (nanopapers). Those are self-supporting networks of entangled CNTs hold together by Van der Waals interactions at the tube-tube junctions. Lu et al. described such three-dimensional self-assembled MWCNTs nanopaper developed using hydrophilic polycarbonate membrane synthesized by controlled pressure vacuum deposition [55]. The obtained highly conductive continuous and compact network was combined with styrene-based SMP, thus facilitating the electrically heating of the nanocomposite. It was of interest to remark that the electrical stimulation (35 V) allowed to drive up a 5 g mass object from 0 to 30 mm in height (Figure 8A) and the material acted as a sensor that responded to the changes in degree of humidity (the electrical resistivity of materials increased with the water content in the sample after immersion). Macromolecular self-assembled MWCNTs structures offer an opportunity to produce percolating conductive network for sensors, controllable devices and deployable structures application [56]. However, an even better dispersion of the nanofillers can be achieved by their surface chemical modifications as reported by Raja et al. [57]. In the PU-based nanocomposites the morphological characterization of the materials revealed good dispersion level for the due to the improved interfacial interaction between the polymer macromolecules and the MWCNTs. Moreover, the PU/PVDF films got improved tensile strength and dynamic storage modulus, as well as good electrical and thermal conductivity. The shape-memory behavior of "U" shaped structures showed R_r of 95% upon constant voltage (40 V).

Another set of SMNCs with good performance indicators were obtained using triethanolamine-functionalized MWCNTs (TEA-f-MWCNTs, MWCNTs up to 2 wt%) by using hyperbranched polyurethanes (HPUs) as polymer matrix [58]. Taking advantage of the strong interfacial interaction of TEA-f-MWCNTs with the PU chains (hydrogen bonding and polar-polar interactions), it was possible to reach significant thermal stability

accompanied with increased degree of crystallinity, enhanced tensile strength (28.5 MPa) and scratch resistance (7 kg). Combining two or more electrically sensitive nanofillers, such as carboxylic acid-functionalized CNTs grafted onto the CNFs and then self-assembled, was an elegant way to generate Joule heating shape recovery [59].

Recently, the effect of epoxy-*graft*-polyoxyethylene octyl phenyl ether (EP-*g*-TX100) on the processing and t-SME of the novel CNT/water-borne epoxy (WEP) nanocomposites was investigated [60]. The introduction of EP-*g*-TX100 in homogenous way in the CNT-epoxy system renders possible the design of the SMP materials with good mechanical properties and two- and triple-shape-memory properties (Figure 8B). Surface (MW)CNTs decoration with metals (Cu, Fe, Ag and Pt) was yet another promising and simple method to nanoreinforce and electrically actuate the SMNCs (Cu-CNT were incorporated in polylactic acid (PLA)/epoxidized soybean oil [61], Fe-MWCNTs and Ag-MWCNTs in PUs [62], combining them with boron nitride [63] or coating of the electrical nanofillers with conductive polymer (polypyrrole-coated MWCNTs) [64].

An effective way to enlarge the practical applications of nanotubes is to assemble them into highly aligned structures for electroactive polymer (EAP) actuator systems [65]. One of the most important classes of EAPs are the electrothermal actuators (ETAs), due to having low driving voltage and being electrolyte-free. Large-area CNT buckypaper (BP, layers of aligned CNT array) as flexible electrode for CNTs loaded double-layer ETA (BP and polydimethylsiloxane layers) has already been studied [66]. It was established that directional control ETAs bending is possible: bending to the BP sides along the length direction of the U-shaped electrodes, and larger deformation of the horizontally cut actuator (CNTs alignment perpendicular to the U-shaped BP band; Figure 9A). This concept gave the idea for potential bionic actuation similar in behavior acting to a human-hand with long service life (Figure 9B).

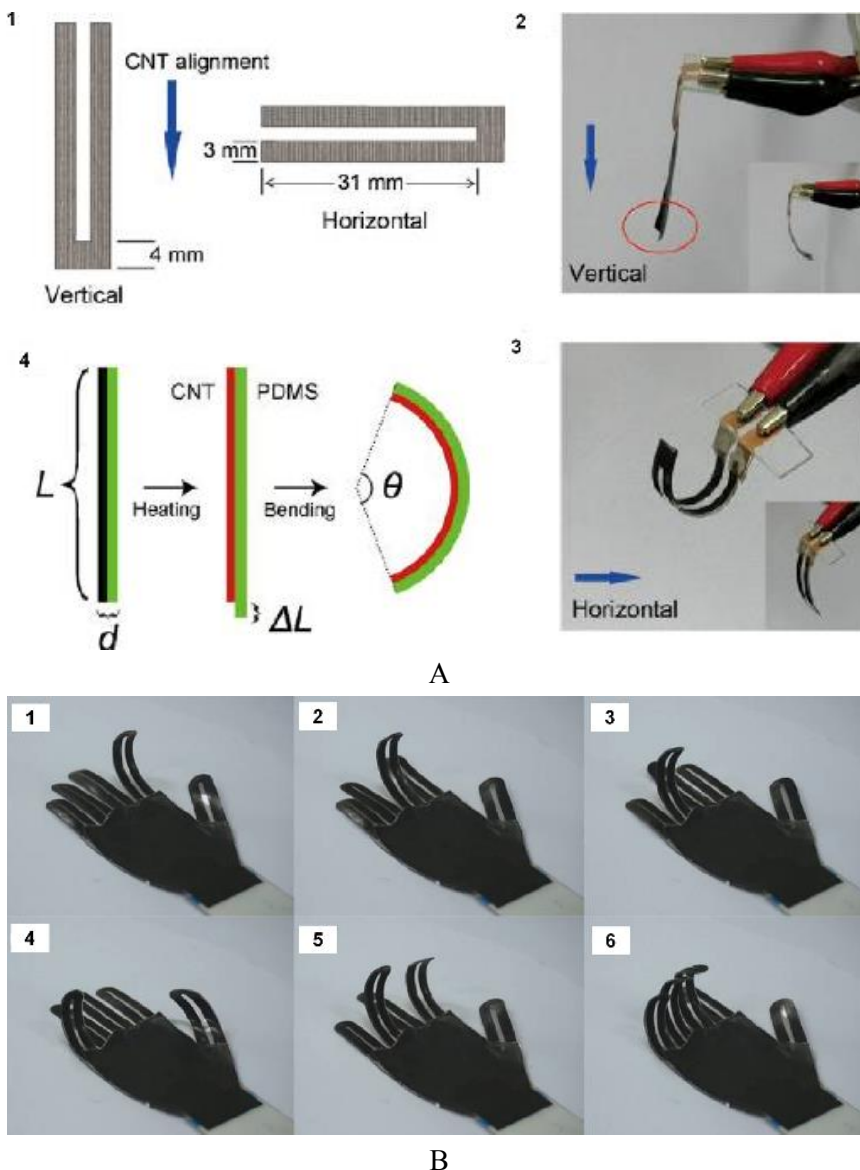Figure 8. Electrically actuated SMNCs containing (MW)CNTs [55, 60].

A

B

Figure 9. SMNCs bilayer structure containing A nanopaper and actuated under electrical current and B [66].

CNFs are also remarkable with their excellent thermal and electrical conductivity, but better interfacial bonding can be obtained after their surface oxidation [67]. Good dispersion of these nanofillers can be achieved by high-power sonication or by *in situ* polymerization and lamination onto styrene-based SMPs [22, 68]. Incorporating them in continuous way resulted in epoxy-based SMNCs with high-speed electrical actuation [69]. Here, of importance was the fiber morphology, as well as the nanoscale dimensioning providing the percolating conductive network.

The reinforcement of the polymer matrix and the maintenance of stable physical cross-linking polymer structure was achieved by using CB as nanofiller [70]. Often, loaded with another conductive nanofiller it is homogeneously dispersed and serves as interconnections between carbon fibres [71] or in direct interaction with MWCNT nanopaper and nickel nanostrand [72]. The resulting SMP materials showed great improvement in electrical and thermal conductivity.

The last discussed nanofiller in this section is graphene with chemical properties similar than these of the nanotubes and structure similar with layered nanoclay. It was incorporated by direct mixing with the polymer matrix for PVA water-induced SMP [73], preparation of polymer blends with embedded functionalized graphene (self-healing materials) [74] or PCL-click coupling with graphene sheet (enhanced mechanical and recovery properties) [75]. The synergistic effect of these nanofillers enhanced the bonding between carbon fiber and SMP matrix *via* Van der Waals and covalent cross-links.

3.2. SMNCs with Incorporated Noble Metals

Due to their large specific surface area and strong surface plasmonic resonance (SPR) properties, nanosized noble metals structures such as silver (Ag) and gold (Au) nanoparticles (NPs), nanorods (NRs), nanowiskers (NWs) and nanowires (NWrs) are of great interest for the production of a new generation multi-responsive SMNCs. These structures offer the advantage of absorbing specific wavelength in the range from deep UV to near IR light and to convert remotely the light energy to heat energy (photo-thermal effect) in a non-invasive way. Inspired by these particular properties, a new trend started in the design of SMP materials with a focus on proper wavelength activation and local shape actuation.

3.2.1. SMNCs with Incorporated Gold Nanofillers

During the last decade, Au NPs demonstrated their great potential as not only systems for optically controllable SME but also as agents conferring self-healing properties (SHP) to the polymer materials [76]. Based on their high efficiency, the authors showed that the incorporation of small amount of poly(ethylene glycol)methyl ether functionalized Au NPs (0.003 wt%) to a cross-linked poly(ethylene oxide) (PEO) films was sufficient to grant photo-thermally induced healable and SME properties to the films. Digital images of the self-healing and the light-induced shape recovery process are presented in Figure 10A. Light-sensitive nanocomposites based on poly(β-amino esters) containing Au NRs have been recently developed and presented SME upon local irradiation with IR light and subsequent heating above the polymer T_g and remained cytocompatibility with cells while having mild inflammatory response [77] [78]. Based on published data, it is likely that the near-IR light-sensitive SMP materials can find

biomedical application since the applied irradiation is capable of penetrating body tissue without damaging it.

Au NRs can also be used with great success in the design of light-guided smart windows, light-tracking solar panels, actuators and others. Zheng et al. produce light-responsive SMP micropillar arrays containing PEGylated Au NRs (up to 0.2 mol%) by applying poly(dimethylsiloxane) molding procedure [79]. By simply modifying and playing with the surface topology (bent-temporary shape or unbent micropillar arrays-permanent shape), it is possible to govern the film optical properties: from opaque (bent pillars) to transparent (straight pillars) upon local laser irradiation (5 sec, wavelength of 532 nm; power of 0.3 W, respectively). Material unidirectional wetting was achieved by covering SMP pillars with thin film of Au or Au-palladium [80]. Using small amount of Au NPs (0.5 wt%) enables also the controlled SPR absorption by cross-linked PEO matrix. Multi-step shape recovery was done by the formation of a temperature gradient in the temporary shape inducing anisotropic polymer chain relaxation and strain energy release [81], Figure 10B. By taking advantage of the anisotropic structure of the NRs it was possible to play on the light polarization angle for effective photo-thermal shape control as in the case of PVA/Au NRs (nanofillers of 0.02 wt%) films [82].

3.2.2. SMNCs with Incorporated Silver Nanofillers

As a metal-ligand coordination system, silver can be successfully used for the production of physical cross-linking SMPs structures. In this direction Wang et al. described SMNCs containing Ag ions (3 wt%)-coordination polymer network (isonicotinate-functionalized polyester (PIE) and the pyrazinamide groups) [83]. The degree of cross-linking, rigidity and shape recovery were modulated by simply controlling the amount of the absorbed ions. Moreover, SMP were considered as suitable for smart wound dressings or implants with antibacterial properties against *Escherichia coli* and cytocompatibility with osteoblast cells (Figure 11A).

With their high thermal and electrical conductivity Ag NWrs offer a possibility to produce metallic nanotubes, stretchable and transparent conducting electrodes and semiconductors, organic light-emitting diodes, organic solar cells, touch screens, electrochemical devices, etc. [84]. A major issue in this system is the achievement of homogeneous nanofiller dispersion for conductive percolating network formation. A novel approach in the design of SMNCs are multilayer structures such as bilayer from Ag NWrs and SMPUs [85, 86]. Of great interest was the fact that the bilayer was flexible and highly conductive (DC voltage of 1.5 V) sufficient to turn on the LED upon strain stretching (elongation less than 12% and resistance of 200 Ω/sq), while the fast electro-responsive shape recovery is based on the Joule effect heating. In this context, deformable electronic devices are of interest for wearable displays, solar panels and

non-invasive biomedical devices fabrication subjects of large deformation to cope with body movements. Recently, Ag NWrs were used for highly flexible and transparent SMP bilayer electrodes (diameter of 60 nm and length of 6 μm) made of cross-linked polyacrylate-based light-emitting diodes [87]. The programming of the materials was a result of the shape-memory properties of the cross-linked network upon either compressive strain (bent up to 16% without significant resistance changes) or upon tensile strain (accompanied by a slight resistance increase). In comparison to the classical used indium-doped tin oxide (ITO) anode, the Ag NWrs/polyacrylate electrodes demonstrated slightly higher efficacy of 14 cd/A.
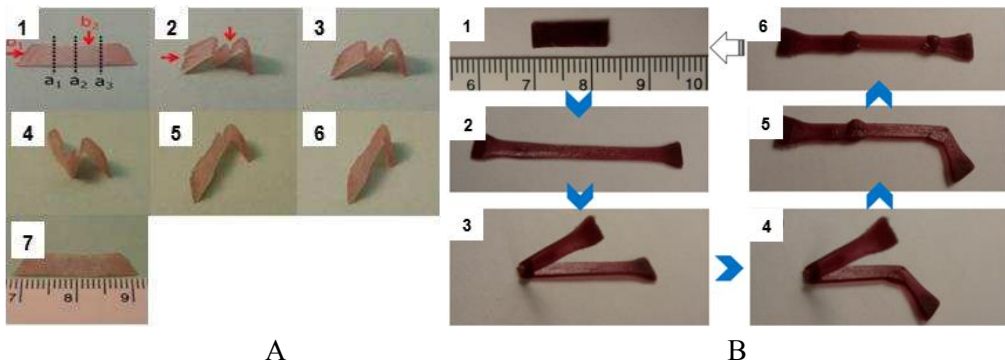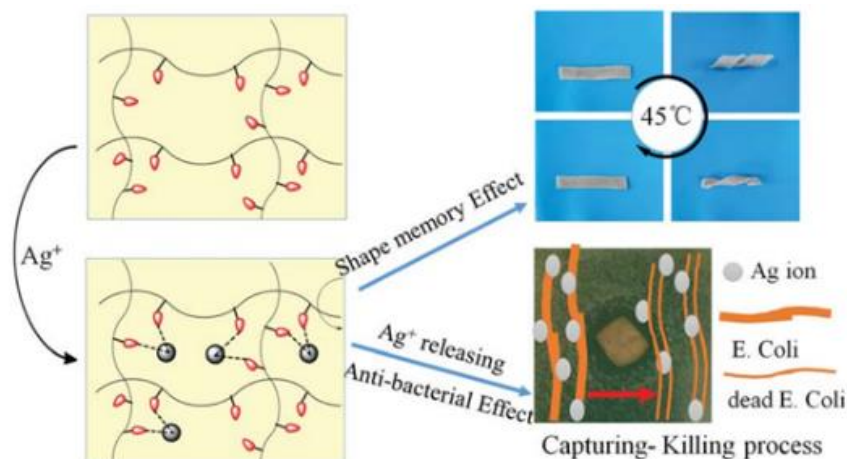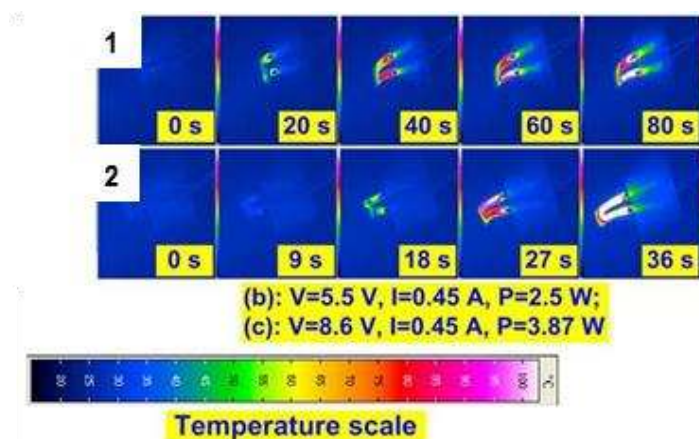

Figure 10. SMNCs materials containig Au nanofillers.

SMNCs embedded with Ag can be of interest for the flexible solar modules (polymer solar cells of semi- transparent solar cells in windows) concept [88]. The nanofiller morphology was a key element for the devices performances (Ag NWrs length) [89]. In their study, Yu et al. showed that (length of 4-10 μm) led to the production of devices with high filling factor (FF or nanowires high surface coverage) but was accompanied with low photo-current (loss of transmittance). In contrast, long Ag NWrs (length above 20 μm) were responsible for high photo-current but lower FF.

Several studies have dealt with the concept of combining multiple nanofillers in one multilayer SMNC for final synergetic effect [90, 91]. Indeed, epoxy-based thermoset SMP resin possessed enhanced electro-thermal properties and electro-activated shape recovery performance, where Ag NPs were decorated graphene oxide (GO) assembly grafted onto carbon fibers. The guiding force for the material shape recovery, resulted in Joule-heating induced process: the self-assembled GO grafted onto the carbon fibers acted as a Joule-heat-carrying layer and the Ag-NPs-decorated GO decreased the thermal dissimilarity and facilitate heat-transfer from the carbon fiber to the polymer matrix. As presented in Figure 11B(2), the SME was faster for nanofiller containing films (36 sec, DC of 8.6 V with temperature range above the polymer T_g).

Figure 11. SMNCs materials contaning Ag nanofillers.

3.3. SMNCs with Incorporated Metal Oxide Nanofillers

Magnetically addressable SMPs are another interesting system, where magnetic NPs play the role of inductive heaters offering the possibility to remotely trigger the shape [92]. This kind of stimuli is of particular importance for the design of biomedical devices where it becomes possible to achieve a noncontact harmless activation of the polymer parts without heating the surround tissue [93]. Good candidates in this section are the iron oxides (Fe_3O_4) NPs, characterized with good biocompatibility and high magnetism. A whole set of possible applications opens up - the fabrication of drug targeting systems, magnetic resonance imaging for clinical diagnosis, recording materials catalysts, magnetically controlled smart implants, etc.

To overcome the general problem of NPs homogeneous dispersion in the material, their surface can be somewhat (non)covalently modified in order to enhance their miscibility within the material and create nanoscale net-points in the polymer matrix. Fe_3O_4 NPs produced from co-precipitation (divalent and trivalent iron salts) using PEG-10000 as dispersing surfactant were uniformly loaded in the biocompatible poly(D,L-lactide) (PDLLA/Fe_3O_4 weight ratios of 1:1, 2:1, 3:1). The key element in this step was the hydrogen bonding between Fe-OH group of Fe_3O_4 and C=O of the polyester resulting in enhanced tensile properties and SME activated upon alternating magnetic field (frequency of 20 kHz and strength of 6.8 kA/m) [94]. Fe_3O_4 NPs (up to 20 wt%) can be synthesized by co-precipitation method by modifying their surface with oleic acid. A clear improvement of the PLLA mechanical properties in terms of elastic modulus, tensile strength and elongation at break was noticed. The authors demonstrated that the shape recovery ratio in PLLA/Fe_3O_4 (nanofilller content 10 wt%) and the recovery speed in an alternating magnetic field were lower than the one in water at 70°C (Figure 13A) [95]. In the literature, PCL as biocompatible polymer was used for the production of cross-linked thermo- and magnetic-sensitive materials [96, 97]. The addition of Fe_3O_4 was done with the aim to accelerate the materials degree of degradation taking advantage from the hydrophilic nature of the NPs promoting the hydrolysis of the polymer ester bonds. Consequently, SMP permanent domain was altered affecting directly the SME performance. The perspective of implants fabrication with desired life time and shape-memory properties was then demonstrated.

In this aspect, non-toxic, biocompatible and highly hydrophilic polymers such as poly(ethylene glycol) (PEG) or poly(vinyl alcohol) (PVA) can be used as second switching segment to create thermo- and water-triggered SMPs appropriate for biomedical applications. What is more, it was possible to confer magnetically-responsive properties to these systems by adding Fe_3O_4 PEG-modified NPs (5 and 10 wt%) within the polymer matrix with excellent R_f and R_r ratio suitable for biomedical applications where the direct hearting of the material is avoided (electrical current between 400 and 450 A, frequency of 166 kHz; Figure 12).

The idea of NPs chemical modification was explored also by Bai et al. by developing a one-pot synthesis of norbornene-capped super-paramagnetic iron oxide NPs. Successfully, the nanofillers were then integrated (up to 20 wt%) into polynorbornene by ring-opening metathesis polymerization of norbornene [98]. As described by the authors, the aim of the NPs functionalization acted as cross-links and magnetic-induction heaters in the macromolecular network architecture. The nanocomposites had a super-paramagnetic response, with saturation magnetization of around 2 and 5 emu/g for the nanocomposites with 10 and 20 wt% Fe_3O_4, respectively.
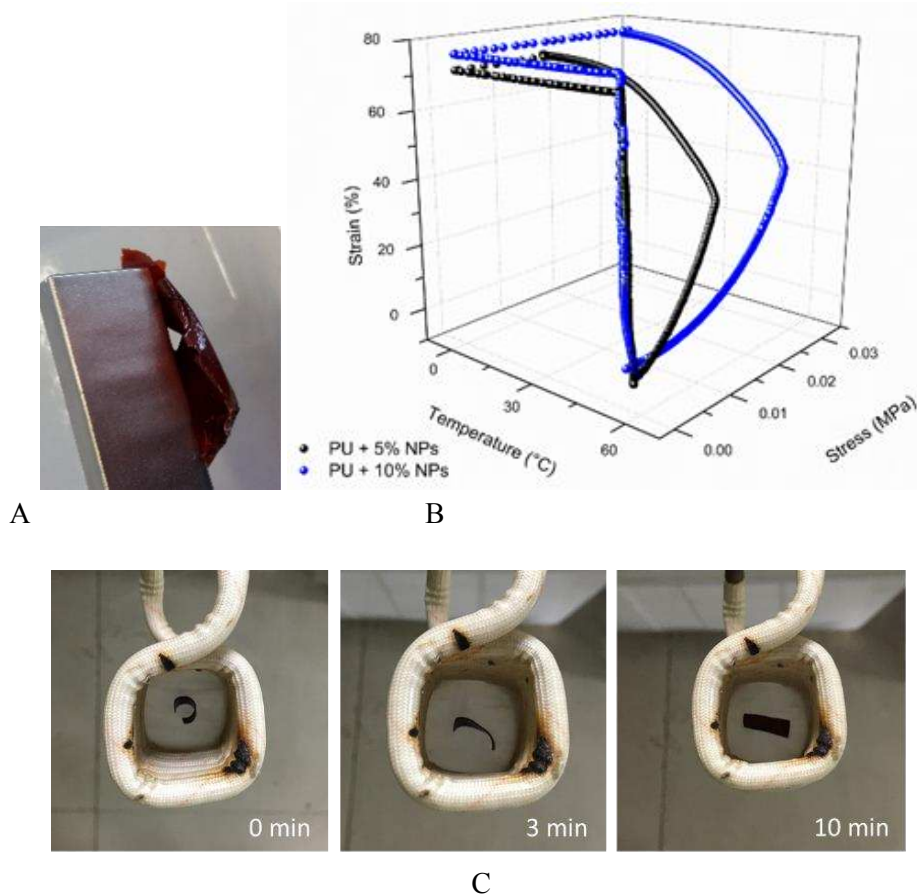
Figure 12. PCL/UPy-based PU materials containing Fe_3O_4-PEG modified NPs with magnetic (A), shape-memory (B) properties activated upon magnetic field (C).

As an effective cross-linking agent Fe_3O_4 NPs was also used for the preparation of the polyPMMA-PEG SMP this time prevented their displacement and reaggregation in the matrix [99]. This setup granted enhanced mechanical properties to the materials accompanied with uniform heat-generation and heat-transfer upon exposure to an alternating magnetic field, when compared to the dispersed NPs. Another approach for better NPs dispersion is to directly graft oligomers on the NPs surface. Good example is the study of Schmidt et al. where oligo(ε-caprolactone)-grafted Fe_3O_4 superparamagnetic NPs were incorporated into thermosets of oligo(ε-caprolactone)dimethacrylate/butyl acrylate: the material recovered its original straight shape in 20 sec (magnetic field frequency of 300 kHz and power of 5.0 kW) [100].

The idea to combine two or more nanofillers in the material was explored also in the case of magnetically triggered devices. In 2014 Li et co-workers obtained SMNCs using biodegradable and biocompatible chemically cross-linked PCL with allyl alcohol as polymer matrix and Fe_3O_4 in order to decorate conductive MWCNTs (Fe_3O_4@M) as a magnetism and electricity responsive source [101]. Covering the outside of the MWCNTs

with magnetic layer enhanced the magnetic properties while the non-coated MWCNTs were responsible for the electric properties of the multi-stimuli responsive material [hot water, magnetic field (frequency of 20 kHz and strength of 6.8 kA/m) and electric field (60 V); Figure 13A]. In addition, the use of semi-crystalline polyester allowed the 2W-reversible shape-memory capabilities when temperature above and below the T_m are applied.

One more group of interesting NPs are the TiO_2 for their semiconductor and photo-catalytic properties, as well as photo-stability in solution, redox selectivity and strong oxidizing power. Up to date, only a few studies focus on the incorporation of TiO_2 NPs for SMNCs fabrication. In the study of Iijima et al. surface-modification of the nanofillers with anionic surfactant is proposed (anionic head group and organic chains are branched into a hydrophobic alkyl and a hydrophilic PEG chain ended by a polymerizable vinyl group) [102]. TiO_2 NPs with the conferred surfactant complex properties gave then stable suspensions in various organic solvents (alcohols, nitriles, ketones and acetates) and polymers [epoxy resin and poly-(methylmethacrylate) resin]. Afterwards, the obtained TiO_2/epoxy nanocomposites were activated via direct heating. Surface-modification of the metal oxide NPs were also done by ring-opening polymerization of ε-caprolactone (g-TiO_2) in order to ensure a good dispersion in the polyester matrix of poly(L-lactide-co-ε-caprolactone) (PLCL). Further physical cross-linking, between the polymer chains of g-TiO_2 and PLCL (TiO_2 of 5 wt%), gave enhanced mechanical properties [103].

Great challenge in the SMNCs chemical architecture is the production of multi-functional materials with shape-memory, SHP and self-cleaning properties (SCP) upon sunlight exposure. Recently it was reported that the combination of TiO_2 NPs and reduced graphene oxide (RGO; up to 1 wt%) can tune easily the materials properties [104]. The high light absorbing capacity of RGO and its energy transfer allowed the heating of the HPU system (close to its T_m) under sunlight exposure and rapid shape recovery (R_r of 91-95%) was recorded (Figure 13B). Here, the nanoreinforced phenomena significantly improved tensile strength, tensile modulus, toughness and elongation at break of the nanocomposites. Of importance in this case was the good dispersion of the nanofiller, its miscibility and interfacial interactions with the polymer chains (presence of hydroxyl groups and polar Ti-O groups).

In the field of metal oxide particles, zinc oxide (ZnO) are attracting also attention for their physical and chemical properties, such as high chemical and photo-stability, good electrochemical coupling coefficient and broad range of radiation absorption. This filler is frequently used for sensor, energy generator and photocatalyst in hydrogen production based on its piezo- and pyroelectric properties. In the literature few articles discuss the ZnO SMNCs dealing with imidazole-zinc ion coordinated shape-memory hydrogel [105], triple-shape-memory poly (acrylonitrile 2-methacryloyloxyethyl phosphorylcholine) based on the dipole–dipole-zinc ion coordination [106] or epoxy-based SMP containing

metallosupramolecular unit formed by coordinating 2,6-bis(*N*-methyl-benzimidazolyl)-pyridine ligands to zinc di[bis(trifluoromethylsulfonyl)-imide] [107], ZnO NRs in PU matrix [108, 109].

A
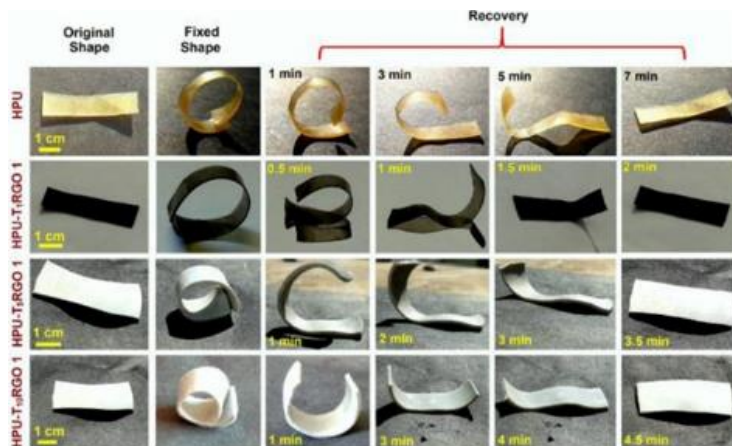
B

Figure 13. SMNCs materials contaning Fe_3O_4 and TiO_2 NPs as nanofillers. Cross-linked PCL SMPs containing Fe_3O_4 decorated with conductive MWCNTs actuated under thermal, magnetic and electrical stimulus (A) [101] and HPU SMNCs materials loaded with TiO_2 NPs with self-healing and shape recovery properties (B) [104].

3.4. SMNCs Containing Cellulose Nanocrystals

Interesting biocompatible nanoreinforcing nanofillers are the cellulose nanocrystals (CNCs, known also as cellulose nanowiskers). This is mainly due to their anisotropic structure (high aspect ratio), renewable resources and stiffness [110]. They are also characterized with relatively low cost, low density, wide bioavailability, renewability and unique physico-chemical properties [111] [112]. The presence of hydroxyl groups in the chemical structure offers a possibility to form supramolecular interactions based on

hydrogen bonding (e.g., SMP higher-modulus as a result of the interconnected CNCs in the polymer matrix) responsible for the water-induced SME. The potential application of such SMNC is reserved for the biomedical field as self-tightening sutures and self-retractable and removable vascular stents fabrication. However, the preparation of nanocomposites by direct incorporation of CNCs into the polymeric matrix remains difficult due to the poor affinity between the hydrophilic nanofiller and the polymer chains. Often the result ends up being an insignificant increase or in some cases a failure to improve the materials physico-mechanical properties.

Interesting approach for the production of thermo-responsive and water- responsive SMNCs by using CNCs as a cross-linking agent is described by Liu et al. [113]. The nanocrystals were chemically bonded *via* their hydroxyl groups to low molecular 4,4-diphenylmethane diisocyanate end-functionalized PCL and PEG. The biocompatible nanocomposite from PEG[60]-PCL[40]-CNC[10] demonstrated excellent thermo- and water-induced SME (R_r of 85%) as presented in Figure 14A. Here, the shape recovery properties depended on the polymer degree of crystallinity and the materials degree of cross-linking.

It is of importance to notice that the CNCs gave the unique possibility to produce water-sensitive SME mechanism which is totally athermal in comparison to traditional systems where water (or other solvent) is used as plasticizers in the idea to lower the polymer T_g. Water-activated mechanically adaptive PU SMNCs with incorporated CNCs have been described in the literature with enhanced mechanical properties (nanofiller content above the percolation limit) [115]. In this flow of ideas, in 2012 Zhu et al. reported an effective strategy to design elastomeric thermoplastic PU/CNCs-based materials with rapid SME response as a result of the successful combination between the nanofiller percolation network (chemo-mechanical adaptability) and the entropic elasticity of the elastomer [116]. The obtained materials were suitable for design of breathable clothing and medical devices triggered by human body liquids. PU-based materials with enhanced tensile strength and the Young's modulus (up to 1040% and 4400%, respectively), were produced from biodegradable poly(glycerol sebacate urethane) (PGSU) were also reported in the literature. This time the nanocrystals were grafted along the polymer macromolecule: CNCs got competed with the -OH groups from PGS prepolymer and reacted with the isocyanate groups of hexamethylene diisocyanate [117]. Blending poly(ethylene glycol)-poly(ε-caprolactone)-based polyurethane (PECU) with functionalized CNCs (pyridine moieties CNC-$C_6H_4NO_2$) can lead to the production of pH-responsive films [114]. The switching units of the materials had attractive interactions from the hydrogen bonding between pyridine groups and hydroxyl moieties: at low pH value the interactions were reduced or disappeared as a result of the pyridine groups protonation (Figure 14B). The final results showed a possibility to produce new smart polymer material (biomaterials, smart actuators, and sensors). CNCs were also incorporated as a hard segment in thermoplastic PU

bionanocomposites [118]. Resulting in thermodynamic incompatibility, between both PU soft/hard segments, microphase separation was obtained and two main T_m transitions were designed. The incorporation of the CNCs led to an increase in the hard phase-degree of crystallinity and improvement of the storage modulus and the shape recovery performances. In other reported data, only 5 wt% CNCs were sufficient to six-fold increase in Young's modulus and five-fold improvement in toughness of poly(mannitol sebacate) making them suitable for biomedical applications as soft tissue engineering scaffolds [119]. In addition, the ureido-pyrimidinone [UPy(OH)$_2$] have the ability to highly dimerize and therefore elaborate a dynamic supramolecular network based on hydrogen bonding in PCL-based PU matrix materials. Introducing CNCs into the PU matrix will allow us the complementary hydrogen bonds with UPy in order to elaborate efficient SMNP-based materials.
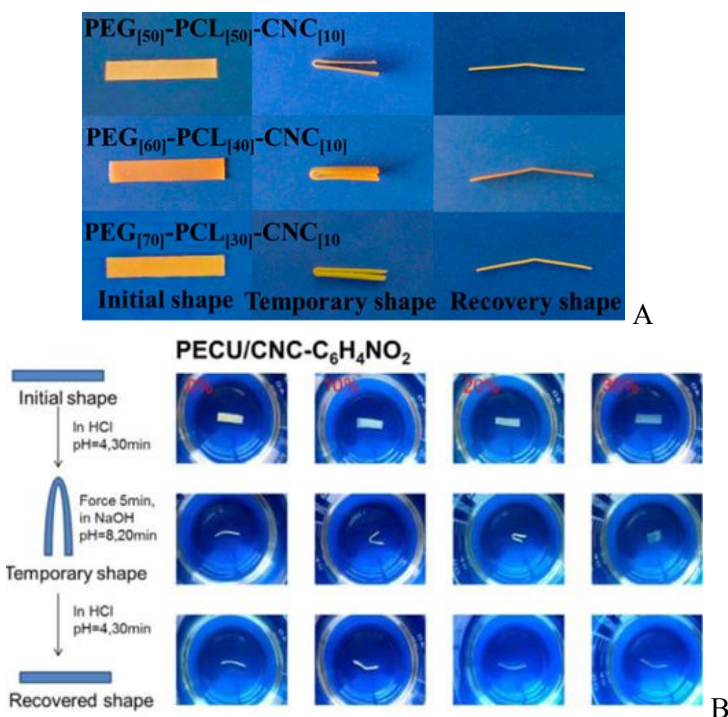

Figure 14. SMNCs materials contaning CNCs: (A) Thermo-responsive shape recovery behavior of the PEG-PCL-CNC nanocomposites when heated in oven at 60°C and (B) digital photos of the shape memory process of PECU/CNC-C$_6$H$_4$NO$_2$ film with different CNC-C$_6$H$_4$NO$_2$ loading immersed in HCl (pH 4) and NaOH (pH 8) solution at room temperature [113] and [114].

In this chapter the authors presented the nanofillers most often used to trigger the polymer materials SME. In the literature SMPs can be reinforced by the incorporation of microfibers, fabrics and Kevlar mats, carbon or glass fibers. Their high elastic modulus, strength and characteristic structural morphology are remarkable and lead to enhanced mechanical load while maintaining the transvers direction [120]. The potential

application of such SMNCs can be suitable for spacecraft self-deployable and vibration control structures [121-123]. Exfoliated nanoclays as part of the hard phase have also positive impact on the materials mechanical properties [124-126]. This is also the case of SiC and SiO_2 and of cross-linking agent with PCL [127] or coupling with SMPU chains [128].

3.5. SMP as Smart 3D Printed Materials

During the last decade the scientific and technological progress has inspired the emergency of exciting 3D printing prototype technologies. As part of the additive manufacturing, stereolithography (SLA) and fused deposition modeling (FDM) techniques, have offered the possibility to expand the polymer materials application at industrial level. Combining the variety of chemical approaches to incorporate functional nanofillers within the polymer matrix and the SMPs "1W-, 2W-" and multi-shape properties, a new trend in the world of material design. SMP quickly found a key place for design of complex deployable structures. Of particular interest is the 4D printing technology where the fourth dimension was added in order to describe the material's transformation (change shape, functionality or properties over time once triggered by an external stimulus) over time [129, 130]. SLA was successfully used as method to use SMP as start material for highly elastic, transparent and electroconductive hydrogels for soft robotics application. [131], composite hydrogels with magnetic responsiveness [132], materials for biocompatible 3D scaffolds as tissue engineering for mesenchymal stem cells culturing [133] or medical devices such as vascular or tracheal stents [134] or methacrylated polycaprolactone precursor, respectively [135]. Materials with tunable SME can be also designed by another method - FDM. Filaments appropriate for 3D printing application from non-commercially available polymers with good processability are now a fact. Rapid prototyping, specific topological structuration and nanodomains formation with long relaxation times of the supramolecular crosslinks [136], as well as devices for object catching and transportation [26] or biomimetic solar tracking sensors or smart solar cell systems [137] can be obtained. The SMP 3D printing approach at structural and material design level is discussed in detail in Chapter 15 of the present book and the readers are kindly invited to consult its contents.

FUTURE DIRECTIONS AND CHALLENGES

SMPs open the door to the production and design of new generation of polymer materials with multi-responsiveness. The possibility to introduce functional nanofillers in the structures offer the unique advantage to enlarge the polymer's application in the yet unexplored field of the practical daily use. Based on current insights, several future directions and related challenges may be considered:

1. The incorporation of different nanostructured fillers in the SMP-matrix allows the enhancement of the materials mechanical properties (unfortunately, staying close to the relatively poor properties of origin). Additional efforts are needed to optimize the nanofillers dispersion and the materials characteristics (structural fatigue, relaxation, creep and duration);

2. Fabrication of biocompatible and biodegradable SMPs medical devices is of great interest for human health. Even if a great range of devices can be produced (scaffolds for tissue engineering, implants for minimally invasive surgery procedures, self-tightening sutures, self-retractable and removable stents, drug delivery systems), the main challenges remain the materials rate of degradation (enzymatic or hydrolytic) their degree of toxicity, mechanical solicitation etc.;

3. Smart materials and structures obtained by three-dimensional manufacturing (3D printing) allow the production of SMNCs as actuators for soft robotics, self-evolving structures, anti-counterfeiting system, active origami and controlled sequential folding. Today, some technological and design limitations are still unsolved, mainly relating to the limited choice of polymers to use, multi-material components fabrication, presence of microstructural defects and materials real time adapting. In this aspect promising efforts are done applying SLA and FDM;

4. Inspired by nature, scientists have designed diverse self-cleaning, self-healing and self-adapting SMPs materials suitable for the elaboration of load-bearing aircraft components, self-cleaning and light-guided windows, flexible solar modules (polymer solar cells), smart textiles, bionic robot etc. However none of those polymer systems is commercially available at present and development of new polymers and polymer blends is still needed;

5. At industrial level, SMP materials can find potential application in automobile engineering (seat and adaptive lens assemblies, reconfigurable storage bins, airflow control devices etc.), polymer solar cells, food packaging for thermal and light sensitive products, deployable structures (reflectors, ground based deployable mirrors), smart textile (life jacket, floating wheels) and others. Yet, the direct transfer from the laboratory to industrial scale remain difficult related to the final SME complexity nature (programming step and the triggering process parameters) in addition to the required quick and versatile manufacturing process, while focusing on use of low-cost additives and ensured profit gain etc.

ACKNOWLEDGMENTS

REFERENCES

[1] http://www.plasticseurope.org/. 2016.

[2] Gandhi, M.V. and Thompson, B.D. (1992). *Smart Materials and Structures.* Springer Netherlands Publisher.

[3] Sun, L., Huang, W., Ding, Z., Zhao, Y., Wang, C., Purnawali, H. and Tnag, C. (2012). Stimulus-responsive shape memory materials: a review. *Materials & Design.* 33: 577-640.

[4] Vernon, L.B. and Vernon, H.M. (1941). *Process of manufacturing articles of thermoplastic synthetic resins*. Google Patents.

[5] Rainer, W., Redding, E., Hitov, J., Sloan, A. and Stewart, W. (1964) *Polyethylene product and process*. US Pat. 3144398.

[6] Huang, W.M., Ding, Z., Wang C.C., Wei, J., Zhao, Y. and Purnawali, H. (2010). Shape memory materials, *Materials Today*, 13: 54-61.

[7] Gunes, I.S. and Jana, S.C. (2008). Shape memory polymers and their nanocomposites: A review of science and technology of new multifunctional materials. *Journal of Nanoscience and Nanotechnology*. 8: 1616-37.

[8] Hornbogen, E. (2006). Comparison of shape memory metals and polymers. *Advanced engineering materials*, 8:101-106.

[9] El Feninat, F., Laroche, G., Fiset, M. and Mantovani, D. (2002). Shape memory materials for biomedical applications. *Advanced Engineering Materials*, 4: 91-104.

[10] Wei, Z.G., Sandstroröm, R. and Miyazaki, S. (1998). Shape-memory materials and hybrid composites for smart systems: Part I Shape-memory materials. *Journal of Materials Sciences,* 33: 3743-3762.

[11] Zhang, F., Zhou, T., Liu, Y. and Leng, J. (2015). Microwave synthesis and actuation of shape memory polycaprolactone foams with high speed. *Scientific reports*, 5 (11152): 1-12.

[12] Du, H., Song, Z., Wang, J., Liang, Z., Shen, Y. and You F. (2015) Microwave-induced shape-memory effect of silicon carbide/poly(vinyl alcohol) composite. *Sensors and Actuators A: Physical*, 228: 1-8.

[13] Fang, Y., Ni, Y., Leo, S.Y., Taylor, C., Basile, V. and Jiang, P. (2015) Reconfigurable photonic crystals enabled by pressure-responsive shape-memory polymers. *Nature Communications*, 6(7416): 1-8.

[14] Fang, Y., Ni, Y., Choi, B., Leo, S.Y., Gao, J., Ge B, Taylor, C., Basile, V. and Jiang, P. (2015) Chromogenic photonic crystals enabled by novel vapor-responsive shape-memory polymers. *Advanced Materials*, 27: 3696-3704.

[15] Guo, W., Lu, C.H., Orbach, R., Wang, F., Qi, X.J., Cecconello, A., Seliktar, D. and Willner, I. (2015). pH-stimulated DNA hydrogels exhibiting shape-memory properties. *Advanced Materials*, 27: 73-78.

[16] Zhao, Q., Qi, H.J. and Xie, T. (2015). Recent progress in shape memory polymer: New behavior, enabling materials, and mechanistic understanding. *Progress in Polymer Science*, 49-50:79-120.

[17] Leng, J., Lan, X., Liu, Y. and Du, S. (2011). Shape-memory polymers and their composites: Stimulus methods and applications. *Progress in Materials Science*.56: 1077-1135.

[18] Lu, H., Lei, M., Yao, Yi., Yu, K. and Fu, Y. (2014) Shape memory polymer nanocomposites: nano-reinforcement and multifunctionalization. *Nanoscience and Nanotechnology Letters*, 6: 772-786.

[19] Gök, M.O., Bilir, M.Z. and Gürcüm, B.H. (2015) Shape-memory applications in textile design. *Procedia - Social and Behavioral Sciences*, 195: 2160-2169.

[20] Sokolowski, W., Metcalfe, A., Hayashi, S., Yahia, L. and Raymond (2007). Medical applications of shape memory polymers. *Biomedical Materials*, 2: S23-S27

[21] Ware, T., Simon, D., Hearon, K., Liu, C., Shah, S., Reeder, J., Khodaparast, N., Kilgard, M. P., Maitland, D. J., Rennaker II, R. L. and Voit, W. E. (2012). Three-dimensional flexible electronics enabled by shape memory polymer substrates for responsive neural interfaces. *Macromolecular Materials and Engineering*, 2012(297):1193-1202.

[22] Haibao, L., Kai, Y., Yanju, L. and Jinsong, L. (2010). Sensing and actuating capabilities of a shape memory polymer composite integrated with hybrid filler. *Smart Materials and Structures*, 19: 1-7.

[23] Mondal, S., Hu, J. L. and Yong, Z. (2006). Free volume and water vapor permeability of dense segmented polyurethane membrane. *Journal of Membrane Science*, 280: 427-432.

[24] Santo, L., Quadrini, F., Accettura, A. and Villadei, W. (2014). Shape memory composites for self-deployable structures in aerospace applications. *Procedia Engineering*, 88: 42-7.

[25] Mao, Y., Yu, K., Isakov, M. S., Wu, J., Dunn, M. L., Qi, J. (2015). Sequential self-folding structures by 3D printed digital shape memory polymers. *Scientific reports*, 5(13616): 1-12.

[26] Yang, Y., Chen, Y., Wei, Y. and Li, Y. (2016). 3D printing of shape memory polymer for functional part fabrication. *The International Journal of Advanced Manufacturing Technology*, 84: 2079-2095.

[27] Huang, W. M., Zhao, Y., Wang, C. C., Ding, Z., Purnawali, H., Tang, J. and Zhang, L. (2012). Thermo/chemo-responsive shape memory effect in polymers: a sketch of working mechanisms, fundamentals and optimization. *Journal of Polymer Research*, 19(9952):1-34.

[28] Behl, M. and Lendlein, A. (2007). Shape-memory polymers. *Materials Today,* 10: 20-28.

[29] Lendlein, A. and Kelch, S. (2002). Shape-memory polymers. *Angewandte Chemie International Edition*, 41: 2034-2057.

[30] Liu, G., Guan, C., Xia, H., Guo, F., Ding, X. and Peng, Y. (2006) Novel shape-memory polymer based on hydrogen bonding. *Macromolecular Rapid Communications*, 27: 1100-1104.

[31] Bellin, I., Kelch, S. and Lendlein, A. (2007). Dual-shape properties of triple-shape polymer networks with crystallizable network segments and grafted side chains. *Journal of Materials Chemistry*, 17: 2885-2891.

[32] Zhang, S., Feng, Y., Zhang, L., Sun, J., Xu, X. and Xu, Y. (2007) Novel interpenetrating networks with shape-memory properties. *Journal of Polymer Science Part A: Polymer Chemistry*, 45: 768-75.

[33] Luo, H., Liu, Y., Yu, Z., Zhang, S. and Li, B. (2008) Novel biodegradable shape memory material based on partial inclusion complex formation between α-cyclodextrin and poly(ε-caprolactone). *Biomacromolecules*, 9: 2573-2577.

[34] Luo, H., Fan, M., Yu, Z., Meng, X., Li, B. and Zhang, S. (2009) Preparation and properties of degradable shape memory material based on partial α-cyclodextrin-poly(ε-caprolactone) inclusion complex. *Macromolecular Chemistry and Physics,* 210: 669-676.

[35] Zhang, S., Yu, Z., Govender, T., Luo, H. and Li, B. (2008). A novel supramolecular shape memory material based on partial α-CD-PEG inclusion complex. *Polymer*, 49: 3205-3210.

[36] Rousseau, I. A. (2008). Challenges of shape memory polymers: A review of the progress toward overcoming SMP's limitations. *Polymer Engineering and Science,* 48: 2075-2089.

[37] Hu, J., Zhu, Y., Huang, H. and Lu, J. (2012). Recent advances in shape–memory polymers: Structure, mechanism, functionality, modeling and applications. *Progress in Polymer Science*, 37:1720-1763.

[38] Ionov L. (2015). Polymeric Actuators. *Langmuir*, 31: 5015-5024.

[39] Pandini, S., Dioni, D., Paderni, K., Messori, M., Toselli, M., Bontempi E. and Riccò, T. (2016). The two-way shape memory behaviour of crosslinked poly(ε-caprolactone) systems with largely varied network density. *Journal of Intelligent Material Systems and Structures*, 27: 1388-1403.

[40] Pandini, S., Passera, S., Messori, M., Paderni, K., Toselli, M., Gianoncelli, A., Bontempi, E. and Riccò, T. (2012). Two-way reversible shape memory behaviour of crosslinked poly(ε-caprolactone). *Polymer*, 53: 1915-1924.

[41] Ishida, K. and Yoshie, N. (2008). Two-way conversion between hard and soft properties of semicrystalline cross-linked polymer. *Macromolecules*, 41: 4753-4757.

[42] Chung, T., Romo-Uribe, A. and Mather, P. T. (2008). Two-way reversible shape memory in a semicrystalline network. *Macromolecules*, 41: 184-192.

[43] Küpfer, J. and Finkelmann, H. (1991). Nematic liquid single crystal elastomers. *Rapid Communications,* 12: 717-726.

[44] Thomsen, D. L., Keller, P., Naciri, J., Pink, R., Jeon, H., Shenoy, D and Ratna B. R. (2001). Liquid crystal elastomers with mechanical properties of a muscle. *Macromolecules*, 34: 5868-5875.

[45] Qin, H., Mather and P. T. (2009). Combined one-way and two-way shape memory in a glass-forming nematic network. *Macromolecules*, 42: 273-280.

[46] Liu, C., Chun, S. B., Mather, P.T., Zheng, L., Haley, E. H. and Coughlin, E. B. Chemically cross-linked polycyclooctene: Synthesis, characterization, and shape memory behavior. *Macromolecules* 35: 9868-9874.

[47] Zotzmann, J., Behl, M., Hofmann, D. and Lendlein A. (2010). Reversible triple-shape effect of polymer networks containing polypentadecalactone-and poly (ε-caprolactone)-segments. *Advanced Materials,* 22: 3424-3429.

[48] Raquez, J. M., Vanderstappen, S., Meyer, F., Verge, P., Alexandre, M., Thomassin, J. M., Jérôme, C. and Dubois, P. (2011) Design of cross-linked semicrystalline poly(ε-caprolactone)-based networks with one-way and two-way shape-memory properties through Diels–Alder Reactions. *Chemistry - A European Journal*, 17: 10135-10143.

[49] Behl, M., Kratz, K., Zotzmann, J., Nöchel, U. and Lendlein, A. (2013). Reversible bidirectional shape-memory polymers. *Advanced Materials,* 25: 4466-4469.

[50] Behl, M., Kratz, K., Noechel, U., Sauter, T. and Lendlein A. (2013). Temperature-memory polymer actuators. *Proceedings of the National Academy of Sciences*, 110: 12555-12559.

[51] Wu, Y., Hu, J., Han, J., Zhu, Y., Huang, H., Li, J. and Tang, B. (2014). Two-way shape memory polymer with "switch-spring" composition by interpenetrating polymer network. *Journal of Materials Chemistry A.*, 2: 18816-18822.

[52] Yao. Z., Kane, C. L. and Dekker, C. (2000). High-field electrical transport in single-wall carbon nanotubes. *Physical Review Letters*, 84: 2941-2944.

[53] Iijima, S., Brabec, C., Maiti, A. and Bernholc, J. (1996). Structural flexibility of carbon nanotubes. *The Journal of Chemical Physics,* 104: 2089-2092.

[54] Lu, H., Yao, Y. and Lin, L. (2013). Carbon-based reinforcement in shape-memory polymer composite for electrical actuation. *Pigment & Resin Technology,* 43: 26-34.

[55] Lu, H., Liu, Y., Gou, J., Leng, J. and Du S. (2011). Surface coating of multi-walled carbon nanotube nanopaper on shape-memory polymer for multifunctionalization. *Composites Science and Technology*, 71: 1427-1434.

[56] Lu, H. and Gou J. (2012). Fabrication and electroactive responsive behavior of shape–memory nanocomposite incorporated with self-assembled multiwalled carbon nanotube nanopaper. *Polymers for Advanced Technologies*, 23: 1529-1535.

[57] Raja, M., Ryu, S. H. and Shanmugharaj, A. M. (2014). Influence of surface modified multiwalled carbon nanotubes on the mechanical and electroactive shape memory properties of polyurethane (PU)/poly(vinylidene diflouride) (PVDF) composites. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 450: 59-66.

[58] Kalita, H. and Karak, N. (2014). Hyperbranched polyurethane/triethanolamine functionalized multi-walled carbon nanotube nanocomposites as remote induced smart materials. *Polymer International*, 63: 1295-1302.

[59] Lu, H. and Min Huang, W. (2013). Synergistic effect of self-assembled carboxylic acid-functionalized carbon nanotubes and carbon fiber for improved electro-activated polymeric shape-memory nanocomposite. *Applied Physics Letters,* 102: 231910-2319104.

[60] Dong, Y., Xia, H., Zhu, Y., Ni, Q. Q. and Fu, Y. (2015). Effect of epoxy-graft-polyoxyethylene octyl phenyl ether on preparation, mechanical properties and triple-shape memory effect of carbon nanotube/water-borne epoxy nanocomposites. *Composites Science and Technology*, 120: 17-25.

[61] Alam, J., Khan, A., Alam, M. and Mohan, R. (2015). Electroactive Shape Memory Property of a Cu-decorated CNT Dispersed PLA/ESO Nanocomposite. *Materials*, 8: 6391-6400.

[62] Raja, M., Shanmugharaj, A. M., Ryu, S. H. and Subha, J. (2011). Influence of metal nanoparticle decorated CNTs on polyurethane based electro active shape memory nanocomposite actuators. *Materials Chemistry and Physics*, 129: 925-931.

[63] Lu, H., Yao, Y., Huang, W. M., Leng, J. and Hui, D. (2014). Significantly improving infrared light-induced shape recovery behavior of shape memory polymeric nanocomposite via a synergistic effect of carbon nanotube and boron nitride. *Composites Part B: Engineering*, 62: 256-261.

[64] Sahoo, N. G., Jung, Y. C., Yoo, H.J. and Cho, J.W. (2007). Influence of carbon nanotubes and polypyrrole on the thermal, mechanical and electroactive shape-memory properties of polyurethane nanocomposites. *Composites Science and Technology,* 67: 1920-1929.

[65] Falvo, M. R., Clary, G. J., Taylor, R. M., Chi, V., Brooks, F.P., Washburn, S. and Superfine, R. (1997). Bending and buckling of carbon nanotubes under large strain. *Nature*, 389: 582-584.

[66] Li, Q., Liu, C., Lin, Y. H., Liu, L., Jiang, K. and Fan, S. (2015). Large-strain, multiform movements from designable electrothermal actuators based on large highly anisotropic carbon nanotube sheets. *ACS Nano*, 9: 409-418.

[67] Gunes, I. S., Jimenez, G. A. and Jana, S. C. (2009). Carbonaceous fillers for shape memory actuation of polyurethane composites by resistive heating. *Carbon*, 47: 981-997.

[68] Haibao, L., Yanju, L., Jihua, G., Jinsong, L. and Shanyi, D. (2010). Electrical properties and shape-memory behavior of self-assembled carbon nanofiber nanopaper incorporated with shape-memory polymer. *Smart Materials and Structures*, 19: 075021-075028.

[69] Luo, X. and Mather, P. T. (2010). Conductive shape memory nanocomposites for high speed electrical actuation. *Soft Matter*, 6: 2146-2149.

[70] Li, F., Qi, L., Yang, J., Xu, M., Luo, X. and Ma, D. (2000). Polyurethane/conducting carbon black composites: Structure, electric conductivity, strain recovery behavior, and their relationships. *Journal of Applied Polymer Science*, 75: 68-77.

[71] Leng, J., Lv, H., Liu, Y. and Du, S. (2007). Electroactivate shape-memory polymer filled with nanocarbon particles and short carbon fibers. *Applied Physics Letters*, 91: 144105-144108.

[72] Lu, H., Gou, J., Leng, J. and Du, S. (2011). Magnetically aligned carbon nanotube in nanopaper enabled shape-memory nanocomposite for high speed electrical actuation. *Applied Physics Letters*, 98: 174105-174108.

[73] Qi, X., Yao, X., Deng, S., Zhou, T. and Fu, Q. (2014). Water-induced shape memory effect of graphene oxide reinforced polyvinyl alcohol nanocomposites. *Journal of Materials Chemistry A*, 2: 2240-2249.

[74] Xiao, X., Xie, T. and Cheng, Y.T. (2010). Self-healable graphene polymer composites. *Journal of Materials Chemistry*, 20: 3508-3514.

[75] Yadav, S. K., Yoo, H. J. and Cho, J. W. (2013). Click coupled graphene for fabrication of high-performance polymer nanocomposites. *Journal of Polymer Science Part B: Polymer Physics*, 51: 39-47.

[76] Zhang, H. and Zhao, Y. (2013). Polymers with Dual Light-Triggered Functions of Shape Memory and Healing Using Gold Nanoparticles. *ACS Appl Mater Interfaces*, 5: 13069-13075.

[77] Hribar, K. C., Metter, R. B. and Burdick, J. A. (2009). Novel nano-composite biomaterials that respond to light. *Departmental Papers*, 2009: 2409- 2411.

[78] Hribar, K. C., Lee, M. H., Lee, D. and Burdick, J. A. (2011). Enhanced release of small molecules from near-Infrared light responsive polymer-nanorod composites. *ACS Nano*, 5: 2948-2956.

[79] Zheng, Y., Li, J., Lee, E. and Yang, S. (2015). Light-induced shape recovery of deformed shape memory polymer micropillar arrays with gold nanorods. *RSC Advances*, 5: 30495-30499.

[80] Chen, C. M., Chiang, C. L. and Yang, S. (2015). Programming tilting angles in shape memory polymer janus pillar arrays with unidirectional wetting against the tilting direction. *Langmuir*, 31: 9523-9526.

[81] Zhang, H., Xia, H. and Zhao, Y. (2014). Light-controlled complex deformation and motion of shape-memory polymers using a temperature gradient. *ACS Macro Letters*, 3: 940-943.

[82] Zhang, H., Zhang, J., Tong, X., Ma, D. and Zhao, Y. (2013). Light Polarization-controlled shape-memory polymer/gold nanorod composite. *Macromolecular Rapid Communications,* 34: 1575-1579.

[83] Wang, L., Wang, W., Di, S., Yang, X., Chen, H., Gong, T. and Zhou, S. (2014). Silver-coordination polymer network combining antibacterial action and shape memory capabilities. *RSC Advances*, 4: 32276-32282.

[84] Dinh, D. A., Hui, K. N., Hui, K., Kumar, P. and Singh, J. (2013). Silver nanowires: a promising transparent conducting electrode material for optoelectronic and electronic applications *Reviews in Advanced Sciences and Engineering*, 2: 1-22.

[85] Luo, H., Li, Z., Yi, G., Wang, Y., Zu, X., Wang, H., H. Huang and Z. Liang (2015). Temperature sensing of conductive shape memory polymer composites. *Materials Letters*, 140: 71-74.

[86] Luo, H., Li, Z., Yi, G., Zu, X., Wang, H., Wang, Y., Huang, H., Hu, J., Liang, Z. and Zhong, B. (2014) Electro-responsive silver nanowire-shape memory polymer composites. *Materials Letters*, 134: 172-175.

[87] Yu, Z., Zhang, Q., Li, L., Chen, Q., Niu, X., Liu, J. and Pei, Q. (2011). Highly flexible silver nanowire electrodes for shape-memory polymer light-emitting diodes. *Advanced Materials*, 23: 664-668.

[88] Li, G., Zhu, R. and Yang, Y. (2012). Polymer solar cells. *Nature Photonics,* 6: 153-161.

[89] Yu, Z., Li, L., Zhang, Q., Hu, W. and Pei, Q. (2011). Silver nanowire-polymer composite electrodes for efficient polymer solar cells. *Advanced Materials,* 23: 4453-4457.

[90] Haibao, L., Fei, L., Jihua, G., Jinsong, L. and Shanyi, D. (2014). Synergistic effect of Ag nanoparticle-decorated graphene oxide and carbon fiber on electrical actuation of polymeric shape memory nanocomposites. *Smart Materials and Structures*, 23: 085034-085041.

[91] Lu, H., Zhu, S., Yang, Y., Huang, W. M., Leng, J. and Du, S. (2015). Surface grafting of carbon fibers with artificial silver-nanoparticle-decorated graphene oxide for high-speed electrical actuation of shape-memory polymers. *Journal of Applied Polymer Science*, 132: 41673-41680.

[92] Mohr, R., Kratz, K., Weigel, T., Lucka-Gabor, M., Moneke, M. and Lendlein, A. (2006). Initiation of shape-memory effect by inductive heating of magnetic nanoparticles in thermoplastic polymers. *Proceedings of the National Academy of Sciences of the United States of America,* 103(10): 3540-3545.

[93] Langer, R. and Tirrell, D. A. (2004). Designing materials for biology and medicine, *Nature*, 428: 487-492.

[94] Zheng, X., Zhou, S., Xiao, Y., Yu, X., Li, X. and Wu, P. (2009). Shape memory effect of poly(D,L-lactide)/Fe_3O_4 nanocomposites by inductive heating of magnetite particles. *Colloids and Surfaces B: Biointerfaces*, 71: 67-72.

[95] Zhang, X., Lu, X., Wang, Z., Wang, J. and Sun, Z. (2013). Biodegradable shape memory nanocomposites with thermal and magnetic field responsiveness. *Journal of Biomaterials Science, Polymer Edition*, 24: 1057-1070.

[96] Yu, X., Zhou, S., Zheng, X., Xiao, Y. and Guo, T. (2009). Influence of *in vitro* degradation of a biodegradable nanocomposite on its shape memory effect. *The Journal of Physical Chemistry* C., 113: 17630-17635.

[97] Yu, X. J., Zhou, S. B., Zheng, X. T., Guo, T., Xiao, Y. and Song, B. T. (2009). A biodegradable shape-memory nanocomposite with excellent magnetism sensitivity. *Nanotechnology*, 20: 235702-235711.

[98] Bai, S., Zou, H., Dietsch H., Simon, Y. C. and Weder, C. (2014). Functional iron oxide nanoparticles as reversible crosslinks for magnetically addressable shape-memory polymers. *Macromolecular Chemistry and Physics*, 215: 398-404.

[99] Shuang, X., Xingjian, L., Yaru, W., Yi, P., Zhaohui, Z., Xiaobin, D. and Yuxing, P. (2014). A remote-activated shape memory polymer network employing vinyl-capped Fe_3O_4 nanoparticles as netpoints for durable performance. *Smart Materials and Structures*, 23: 085005-085012.

[100] Schmidt, A. M. (2006). Electromagnetic activation of shape memory polymer networks containing magnetic nanoparticles. *MMacromolecular Rapid Communications*, 27: 1168-1172.

[101] Li, W., Liu, Y. and Leng, J. (2014). Shape memory polymer nanocomposite with multi-stimuli response and two-way reversible shape memory behavior. *RSC Advances*, 4: 61847-61854.

[102] Iijima, M., Kobayakawa, M., Yamazaki, M., Ohta, Y. and Kamiya, H. (2009). Anionic surfactant with hydrophobic and hydrophilic chains for nanoparticle dispersion and shape memory polymer nanocomposites. *Journal of the American Chemical Society*, 131: 16342-16343.

[103] Lu, X. L., LÜ, X. Q., Wang, J. Y., Sun, Z. J., Tong, Y. X. (2013), Preparation and shape memory properties of TiO₂/PLCL biodegradable polymer nanocomposites. *Transactions of Nonferrous Metals Society of China*, 23: 120-127.

[104] Thakur, S. and Karak, N. (2015). Tuning of sunlight-induced self-cleaning and self-healing attributes of an elastomeric nanocomposite by judicious compositional variation of the TiO₂-reduced graphene oxide nanohybrid. *Journal of Materials Chemistry A*, 3: 12334-12342.

[105] Nan, W., Wang, W., Gao, H. and Liu, W. (2013). Fabrication of a shape memory hydrogel based on imidazole–zinc ion coordination for potential cell-encapsulating tubular scaffold application. *Soft Matter*, 9: 132-137.

[106] Han, Y., Bai, T., Liu, Y., Zhai, X. and Liu, W. (2012). Zinc ion uniquely induced triple shape memory effect of dipole–dipole reinforced ultra-high strength hydrogels. *Macromolecular Rapid Communications*, 33: 225-231.

[107] Wu, Y., Hu, J., Zhang, C., Han, J., Wang, Y. and Kumar, B. (2015). A facile approach to fabricate a UV/heat dual-responsive triple shape memory polymer. *Journal of Materials Chemistry A*, 3: 97-100.

[108] Kumpfer, J. R. and Rowan, S. J. (2011). Thermo-, photo-, and chemo-responsive shape-memory properties from photo-cross-linked metallo-supramolecular polymers. *Journal of the American Chemical Society*, 133: 12866-12874.

[109] Koerner, H., Kelley, J., George, J., Drummy, L., Mirau, P., Bell, N. S., Hsu, J. W. P. and Vaia, R. A. (2009). ZnO nanorod−thermoplastic polyurethane nanocomposites: *Morphology and Shape Memory Performance. Macromolecules*, 42: 8933-8942.

[110] Habibi, Y., Lucia, L. A. and Rojas, O. J. (2010), Cellulose nanocrystals: chemistry, self-assembly, and applications. *Chemical Reviews*, 110: 3479-3500.

[111] Šturcová, A., Davies, G. R., Eichhorn, S. J. (2005). Elastic modulus and stress-transfer properties of tunicate cellulose whiskers. *Biomacromolecules*, 6: 1055-1061.

[112] Mendez, J., Annamalai, P. K., Eichhorn, S. J., Rusli, R., Rowan, S. J., Foster, E. J. and Weder C. (2011). Bioinspired Mechanically Adaptive Polymer Nanocomposites with Water-Activated Shape-Memory Effect. *Macromolecules*, 44: 6827-6835.

[113] Liu, Y., Li, Y., Yang, G., Zheng, X. and Zhou, S. (2015). Multi-stimulus-responsive shape-memory polymer nanocomposite network cross-linked by cellulose nanocrystals. *ACS Applied Materials and Interfaces*, 7: 4118-4126.

[114] Li, Y., Chen, H., Liu, D., Wang, W., Liu, Y. and Zhou, S. (2015). pH-responsive shape memory poly(ethylene glycol)–poly(ε-caprolactone)-based polyurethane/ cellulose nanocrystals nanocomposite. *ACS Applied Materials and Interfaces*, 7: 12988-12999.

[115] Mendez, J., Annamalai, P. K., Eichhorn, S. J., Rusli, R., Rowan, S. J., Foster, E. J. and Weder, C. (2011). Bioinspired mechanically adaptive polymer nanocomposites with water-activated shape-memory effect. *Macromolecules*, 44: 6827-6835.

[116] Zhu, Y., Hu, J., Luo, H., Young, R. J., Deng, L., Zhang, S., Fan, Y. and Ye, G. (2012). Rapidly switchable water-sensitive shape-memory cellulose/elastomer nano-composites. *Soft Matter*. 8: 2509-2517.

[117] Wu, T., Frydrych, M., O'Kelly, K. and Chen, B. (2014). Poly(glycerol sebacate urethane)-cellulose nanocomposites with water-active shape-memory effects. *Biomacromolecules*, 15: 2663-2671.

[118] Saralegi, A., Gonzalez, M. L., Valea, A., Eceiza, A., Corcuera, M. A. (2014). The role of cellulose nanocrystals in the improvement of the shape-memory properties of castor oil-based segmented thermoplastic polyurethanes. *Composites Science and Technology*, 92: 27-33.

[119] Sonseca, Á., Camarero-Espinosa, S., Peponi, L., Weder, C., Foster, E. J., Kenny, J. M. and Giménez, E. (2014). Mechanical and shape-memory properties of poly(mannitol sebacate)/cellulose nanocrystal nanocomposites. *Journal of Polymer Science Part A: Polymer Chemistry*, 52: 3123-3133.

[120] Zhang, C. S. and Ni, Q. Q. (2007). Bending behavior of shape memory polymer based laminates. *Composite Structures*, 78: 153-161.

[121] Douglas, C., Mark, L., Mark, S., Emmett, N. and Randal, S. Elastic memory composite material: An enabling technology for future furlable space structures. *46th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference: American Institute of Aeronautics and Astronautics*.

[122] Sen, R., Zhao, B., Perea, D., Itkis, M. E., Hu, H., Love, J., Bekyarova, E. and Haddon, R. C. (2004). Preparation of single-walled carbon nanotube reinforced polystyrene and polyurethane nanofibers and membranes by electrospinning. *Nano Letters*, 4: 459-464.

[123] Lan, X., Liu, Y., Lv, H., Wang, X., Leng, J. and Du, S. (2009). Fiber reinforced shape-memory polymer composite and its application in a deployable hinge. *Smart Materials and Structures*, 18: 024002-024008.

[124] Kim, M. S., Jun, J. K. and Jeong, H. M. Shape memory and physical properties of poly(ethyl methacrylate)/Na-MMT nanocomposites prepared by macroazoinitiator intercalated in Na-MMT. *Composites Science and Technology,* 68: 1919-1926.

[125] Cao, F. and Jana S. C. Nanoclay-tethered shape memory polyurethane nanocomposites. *Polymer,* 48: 3790-800.

[126] Xu, B., Huang, W. M., Pei, Y. T., Chen, Z. G., Kraft, A., Reuben, R., De Hosson J. T. M. and Fu, Y. Q. (2009). Mechanical properties of attapulgite clay reinforced polyurethane shape-memory nanocomposites. *European Polymer Journal*, 45: 1904-1911.

[127] Zhang, Y., Wang, Q., Wang, C. and Wang, T. High-strain shape memory polymer networks crosslinked by SiO_2. *Journal of Materials Chemistry*, 21: 9073-9078.

[128] Park, J. S., Chung, Y. C., Lee, S. D., Cho, J. W., Chun, B. C. (2009). Shape memory effects of polyurethane block copolymers cross-linked by celite. *Fibers and Polymers*, 9: 661-666.

[129] Tibbits, S. (2014). 4D printing: multi-material shape change. *Architectural Design*, 84: 116-121.

[130] Campbell, T. A., Tibbits, S. and Garrett, B. (2014). The programmable world. *Scientific American,* 311(5): 60-65.

[131] Odent, J., Wallin, T. J., Pan, W., Kruemplestaedter, K., Shepherd, R. F. and Giannelis, E. P. (2017). Highly elastic, transparent, and conductive 3D-printed ionic composite hydrogels. *Advanced Functional Materials*, 27: 1701807-1701817.

[132] Hassan, R. U., Jo, S. and Seok, J. (2018). Fabrication of a functionally graded and magnetically responsive shape memory polymer using a 3D printing technique and its characterization. *Journal of Applied Polymer Science*, 135: 45997-56004.

[133] Miao, S., Zhu,. W, Castro, N. J., Nowicki, M., Zhou, X., Cui. H., Fisher J. P. and Zhang L. G. (2016). 4D printing smart biomedical scaffolds with novel soybean oil epoxidized acrylate. *Scientific reports*, 6: 27226-27236.

[134] Zarek, M., Layani, M., Cooperstein, I., Sachyani, E., Cohn, D., Magdassi, S. (2016). 3D printing of shape memory polymers for flexible electronic devices. *Advanced Materials*, 28: 4449-4454.

[135] Zarek, M., Mansour, N., Shapira, S. and Cohn, D. (2017). 4D printing of shape memory-based personalized endoluminal medical devices. *Macromolecular Rapid Communications*, 38: 1600628-1600634.

[136] Senatov, F. S., Niaza, K. V., Zadorozhnyy, M. Y., Maksimkin, A. V., Kaloshkin, S. D. and Estrin, Y. Z. (2016). Mechanical properties and shape memory effect of 3D-printed PLA-based porous scaffolds. *Journal of the Mechanical Behavior of Biomedical Materials*, 57: 139-148.

[137] Yang, H., Leow, W. R., Wang, T., Wang, J., Yu, J., He, K., D. Qi, Wan, C. and Chen, X. (2017). 3D printed photoresponsive devices based on shape memory composites. *Advanced Materials*, 29: 1701627-1701634.