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Feature Article

Shape-memory polymers for multiple applications in the materials world

Florence Pilate [a,1], Antoniya Toncheva [a,b,1], Philippe Dubois [a], Jean-Marie Raquez [a,*]

[a] Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers, University of Mons, Place du Parc 20, B-7000 Mons, Belgium
[b] Laboratory of Bioactive Polymers, Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St, bl. 103A, BG-1113 Sofia, Bulgaria

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ABSTRACT

Shape-memory polymers (SMPs) as stimuli-responsive shape-changing polymers are of great interest for fundamental research and technological innovation. In this contribution, a brief review of the recent trends in the field of SMPs is presented with particular focus on their structure, shape-memory effects and working mechanism. A special attention is paid to smart multi-responsive and multi-functional SMP materials as emerging technological class. They are mainly described as shape-memory nanocomposites (SMCs) where the incorporation of functional (in)organic nanofillers in the SMP matrices is purposely carried out. Potential applications of the SMCs-based materials as medical and biomimetic devices, self-healing systems, self-deployable structures, actuators, sensors, etc. or their direct implementation in the industry are finally outlined.

Contents

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[*] Corresponding author.
E-mail address: jean-marie.raquez@umons.ac.be (J.-M. Raquez).
[1] F.P. and A.T. contributed equally to this work.

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1. Introduction

An emerging class of new materials is the so-called "shape-memory" composites including shape-memory polymers (SMPs), alloys, hybrids, ceramics and gels. The main focus for the moment falls on SMPs due to a multitude of desirable qualities: low density, potentially recyclable at relatively low cost, high recoverable strain within a wide range of stimuli, transparence, chemical stability and modification, easier processing, biocompatibility and biodegradability with an opportunity to adjust the degradation rate [1]. SMPs also happen to be programmable (multi)stimuli-responsive shape-changing polymers and possess the remarkable property to recover their initial shape upon direct or Joule heating, radiation and laser heating, microwaves [2,3], pressure [4], moisture, solvent or solvent vapors [5] and change in the pH values [6]. Depending on the degree of shapes to acquire the materials may belong to multi-shape or two-way SMPs. The first group refers to materials that are capable to memorize more than one temporary shape with subsequent recovering in a highly controllable irreversible one-way manner. The second one can exhibit programmable and reversible shape switching between two distinct shapes. The growing interest on SMP production is well-highlighted by the increased number of publications during the last fifteen years (Fig. 1, SMPs).

Despite the great range of possible shapes to adopt, a major drawback of the SMPs is their comparatively low tensile strength and stiffness, actuation restricted mostly to heat-related treatment and lack of proper function. Other key-limitations include low thermal conductivity, inertness to electrical, light and electromagnetic stimuli accompanied with slow response ability and low recovery time during actuation. As a result their potential applications are often limited especially when high-performance is required. To overcome these difficulties new generation of shape-memory nanocomposites (SMCs) has been designed [7,8]. Generally, they are produced by the incorporation of one or more (in)organic nanofillers (nanotubes, nanofibers, nanospheres, nanorods, etc.) within the polymer matrix. The advantages of the incorporated nano-reinforcement agents are based on their high specific surface area, high stiffness and their inherent functionalities (electrical conductivities, water-responsive, etc.). Therefore the obtained SMCs can be characterized by improved thermal, mechanical and electrical properties [9]. In most cases they are defined as multi-stimuli-responsive materials with conferred functionality [10,11], a feature which enlarges their implementation as smart textiles and apparels [12], intelligent medical devices [13], flexible electronic devices [14], sensor and actuators [15], high performance water-vapor permeability membranes [16], self-deployable and self-folding structures in spacecraft [17,18], aerospace applications [19] and many others. Nowadays, the SMCs integrally make part of the wave of modern polymer materials innovation, confirmed by the increased number of published scientific articles (Fig. 1, SMCs).

The present review is focusing on the recent developments in the design of SMPs for multi-responsiveness. After a short review of the materials conceptual evolution during the last twenty years, SMCs as new generation polymer materials are thereby highlighted. Their production by the incorporation of nanosized fillers such as carbon-based [carbon nanotubes, carbon fibers, carbon black, graphene], metal oxide nanoparticles (Fe_3O_4, TiO_2 or ZnO), noble metal-based nanostructures (gold and silver), and cellulose nanocrystals is featured. Different approaches on the nanofillers dispersion and stability in the polymer matrix are described and compared. They include direct blending of the nanosized structures within the polymer matrix, nanofillers surface modification and alignment, their cross-linking with the polymer chains as well as conversion into macroscale structures.

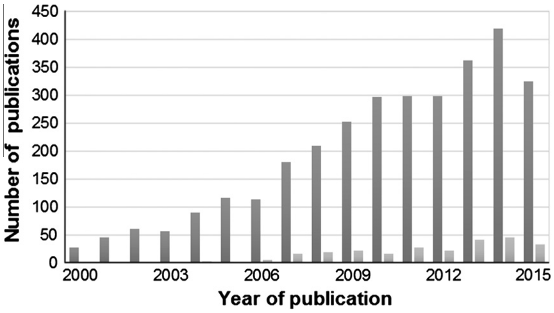

Fig. 1. Number of scientific publications per year on the SMPs (darkest bars) and SMCs (brighter bars). *Source:* Scopus®, Elsevier B.V.; data research made on January, 2016.

2. From basic SMPs to multi-responsive materials

Following the general definition, a SMP is described as a polymer able to memorize its original shape, to acquire a metastable temporary shape upon deformation and to revert back to the permanent shape upon exposition to an appropriate stimulus. This capacity of the polymer to trigger a recovery from a fixed shape to the initial one is called the shape-memory effect (SME) [20]. The ability to fix the temporary shape is quantified by the shape fixity ratio (R_f), while the shape recovery ratio (R_r) represents the extent to get back to the original shape. During the nineteens and early beginning of 2000's, heat-responsive shape-memory poly(ester-urethane)s (SMPURs) were the most investigated systems. Their major actuation is related to a thermal transition, which is often associated to the melting temperature of polymeric matrix (T_m). After the great progress of Leindlein's work in this domain (production of self-tightenable biodegradable suture), new technologies on the materials processing and prototyping allowed the development of more innovative materials with different actuation modes [21]. SMPs can be furthermore actuated by moisture, magnetic field, light and electrical current as additional stimuli. Recently, SMPs have been extended to triple- and multi-responsive concept. Due to the potential as artificial muscles, research has now been leading towards polymer systems with reversible shape-memory properties achieved under stress. In the forthcoming section, heating-responsive SMPs will be briefly described since a great number of reviews has already been published in this field. An emphasis will be made on the evolution of new triggering [especially ultraviolet (UV) light] and new actuation modes (multi-shape SMPs or reversibly actuated polymers) over the last 10 years.

2.1. Dual-shape heating-responsive SMPs

In general, heating-responsive SMPs are characterized by network architecture based on permanent domains (chemical or physical cross-linking) and switching domains associated to a transition temperature (T_{trans}). T_{trans} can be associated to the glass transition temperature (T_g) or T_m of polymer. In order to observe the SME, a programming step is required to fix the temporary shape. Therefore, the deformation (elongation, bending, torsion, etc.) can be obtained by pre-heating the sample above and cooling it below the T_{trans}. After unloading, the fixed temporary shape is obtained and remains stable unless a second heating above T_{trans} is applied. This process is defined as one-way shape-memory effect (1W-SME), whereby only the recovery step (sample contraction) is spontaneous. In addition, when two different shapes are involved during the thermo-mechanical process, these polymers can be also defined as dual-shape SMPs. From the mid-1990s until early 2000s, shape-memory behavior of segmented polyurethanes (PUs), composed of a polyol (soft segment) and a diisocyanate coupled with a chain extender (hard phase), were intensively studied for their flexible molecular design and promising applications. In these systems, hard segments acts as physical cross-links through hydrogen bonds, while switching domains are associated to semi-crystalline polyesters like poly(ε-caprolactone) (PCL) with a T_m of ca. 45 °C (for oligoPCL) [22,23] or to glassy polymers like poly(ethylene adipate) (PEA) glycol (ca. T_g in the range from 5 to 50 °C) [24]. A great number of publications was also focused on the production of SMP materials combining the properties of poly(ester-urethane)s (PURs) and PCL as switching unit [25–28]. In the meantime the shape-memory properties of ethylene oxide-ethylene terephthalate segmented copolymers were also largely studied [29–31]. In 2002 the scientific work of Lendlein and Langer was in fact the spark in the SMP domain, by demonstrating that oligo(ε-caprolactone)- and oligo(*p*-dioxanone)-based PUR can be employed as smart degradable sutures [32]. Since then, scientific interest has intensively grown to more functional SMPs with biodegradable, biocompatible and suitable mechanical properties, namely for complex medical devices such as vascular stents. For example, SMP materials with good biocompatibility were synthesized by Yang et al. using poly(*p*-dioxanone)-*b*-poly(tetramethylene oxide glycol) multiblocky copolymers [33]. Several reviews have thereby addressed the classification of the heating-responsive SMPs depending on the nature of the network (chemical and physical) or of the transition segment (glassy or crystalline domains) [21,34,35], some of them being more specialized in biomedical realm [36,37]. Nowadays, SMPs find larger range of applications such as smart textiles [38], materials for aerospatiale engineering [19,39,40] and others. As a result, materials with new shaping, better processability, capacity to memorize more than one temporary shape and reversible recovery properties are being gradually discovered. In addition, SMPs can be thermally-triggered by indirect heating via Joule effect (e.g., PURs enriched with carbon nanotubes) [41,42], infra-red (IR) irradiation (e.g., cellulose nanocrystals filled thermoplastics elastomers) [43] or magnetically actuated nanocomposites [44–46]. As described in Section 3, most of these actuation modes require the incorporation of functional nanofillers within the polymer matrix. Moisture was also used as an effective stimulus for the shape-memory polyurethane (SMPUs) actuation using the plasticization effect of the solvent with a direct impact on T_g of the polymer [47,48].

2.2. Photo-responsive SMPs

The use of light as stimulus to actuate the SMPs presents several advantages over the heating stimulus approach. For example, a soft activation of SMP materials can be easily executed for biomedical applications by avoiding an undesirable heating/burning at the surrounding tissue during actuation. Another advantage is that remote control at room temperature can be achieved by selecting suitable wavelength, light polarization direction and intensity [49]. Polymer shape-changes, such as contraction and bending, have been observed from more than 30 years in nematic liquid-crystal elastomers containing azobenzene moieties for their *trans-cis* photo-isomerization. One of the first study on polymer film SME was realized by

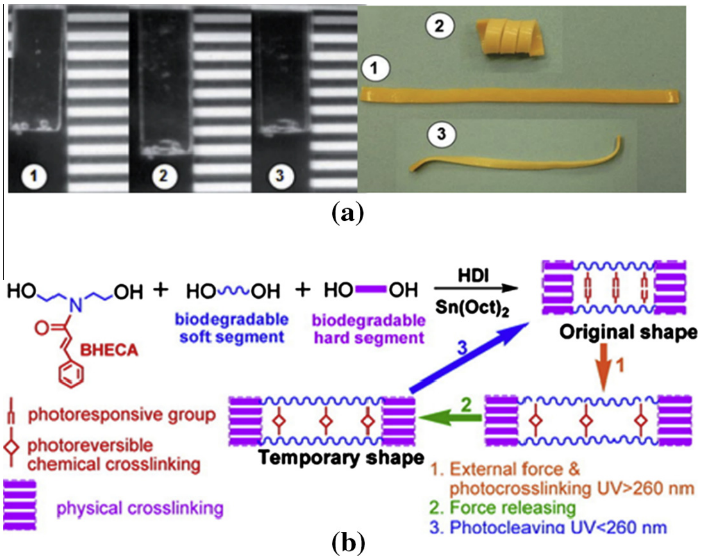

Fig. 2. Digital images of (a) permanent shapes (1), temporary shapes (2) and recovered shapes (3) of CA-grafted polymers networks (left) and IPN-based systems (right), (b) light-SME mechanism in multiblock PURs containing biodegradable segments and pendant photoreactive groups. Adapted with permission from Lendlein et al. [50] copyright 2005 Nature Publishing Group for (a) and from Wu et al. [55] copyright 2011 American Chemical Society for (b).

Lendlein and his co-workers in 2005 [50]. They studied different pre-determined shapes (elongation, arches or spirals) upon UV light illumination. In contrast to the photo-thermal effect, where the light is only used during the sample recovery process and not in the programming of the temporary shape, in the case of the photo-responsive systems the light source allowed to achieve both processes through the presence of photo-sensitive functional groups along the polymer chain [51,52]. For this purpose Lendlein et al. selected cinnamic acid (CA) and cinnamylidene acetic acid (CAA) as photo-responsive switches, being able to undergo photo-reversible [2+2] cycloaddition reaction in function of a certain wavelength. Cyclobutane rings occur by dimerization of the double bonds from two neighbor molecules upon UV light irradiation with specific wavelength ($\lambda < 260$ nm and 300 nm for CA and CAA, respectively). Reverse reaction occurs at $\lambda < 260$ nm for both moieties. Therefore, when the coiled segments of the amorphous polymer chains are elongated by stretching the polymer film, new cross-links in the material are formed upon irradiation and the temporary shape is finally obtained after unloading. This concept was the basis for the production of one of the first SMP system from on CA molecules grafted onto the polymer network made of *n*-butyl acrylate (BA), hydroxyethyl methacrylate (HEMA) and ethylene glycol-1-acrylate-2-CA (HEA-CA) with (propylene glycol)dimethacrylate as cross-linker. As a second approach, they formed an interpenetrated network (IPN) made of BA and loaded with about 20 wt% star-poly(ethylene-glycol) containing CAA end-groups. In both systems, the recovery ratio reached high value (more than 90%) (Fig. 2(a)). As described by Yu and Ikeda, the work of Lendlein's group made a major progress in the field of photo-deformable polymers since this area was sparsely studied up to that moment. However, significant effort still had to be done in terms of structure and potential applications [53]. In 2011 Jin et al. synthesized a diol monomer with a pendant photo-responsive group, *i.e. N,N-bis*-2-(hydroxyethyl)cinnamide (BHECA), following a safe process giving high reaction yield [54]. BHECA was then involved in a two-step condensation reaction using low molecular weight PCL-diol [PCL$(OH)_2$] and poly(L,L-lactide)-diol [PLLA$(OH)_2$] leading to a PUR multiblock of biodegradable segments and pendant photoreactive groups. The permanent network was achieved by physical cross-linking through hard phase of PUR (PLLA) (Fig. 2(b)). For BHECA content of 20 wt%, R_f was of 50% and R_r reached more than 95% with PLLA$(OH)_2$ content of 50 wt% [55]. In 2013, Rochette and Ashby designed new biodegradable PUR pre-polymers having pendant photo-responsive moiety within each repeating unit and consequently offering a uniform distribution along the polymer backbone. Comparatively to the above-mentioned PCL- and PLLA-based PUR, thermal and mechanical properties can be addressed to biomedical applications, where fast degradation rate is needed [56]. They synthesized two diester monomers with cinnamoyl moieties and proceeded to polycondensation reaction with two diols. Hydroxyl-terminated pre-polymers were added onto unsaturated end-groups using 2-isocyanatoethyl methacrylate. Finally, curing in presence of azobisisobutyronitrile resulted in the formation of photo-responsive thermosets with consistent fixity and recovery ratios (50% and 90%, respectively).

2.3. Chemo-responsive SMPs

Chemo-responsive SMPs, pH-, redox- and moisture- and solvent-induced, are one of the barely studied systems in the literature [57–59]. In 2012 Han et al. proposed to use pH as trigger for SMPs for its convenience and safety in medical

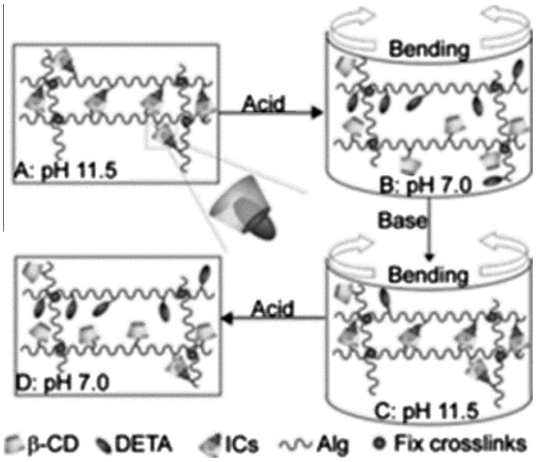

Fig. 3. pH-induced SME in β-CD-DETA inclusion complexes. Adapted with permission from Han et al. [59] copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

applications [59]. On the molecular level, such systems were dual-component, similar to the heating-responsive SMPs. Alginate (Alg) chains cross-linked with calcium cations served as the fixation domain, while the switching domain was constituted of β-cyclodextrin (β-CD) and diethylenetriamine (DETA) when introduced in the Alg matrix. The free-standing hydrogel was obtained by cross-linking carboxyl groups of Alg after addition of calcium chloride solution. At pH 11.5, inclusion complexes between β-CD and DETA were formed. In return, these complexes were dissociated at neutral pH. Based on this assumption, the obtained rigid film was put in neutral solution to provoke the dissociation of the complexes by protonation of the DETA amino group allowing the sample deformation. After this step, the material temporary shape could be fixed by exposure at pH 11.5. Recovery to the original shape was simply obtained by new immersion at pH 7 (see mechanism illustrated in Fig. 3). Since the pH of the human body is close to 7, such stimuli was interesting to be explored for potential implementation of the SMPs as smart medical devices. Later the same research group proposed another novel system, prepared by cross-linking β-cyclodextrin modified chitosan (β-CD-CS) and ferrocene modified branched ethylene imine (Fc-PEI) [58]. The inclusion complexes were formed by interaction between Fc and β-CD (mixing β-CD-CS and Fc-PEI) and served as switching domain. It was possible to dissociate the complex once Fc was in its oxidation state (Fc^+). The redox-responsive SM hydrogel was obtained after cross-linking the polymer chains. Immersion of a plane strip in an oxidative solution, allowed the sample softening as a consequence of the complexes dissociation. Consecutive immersion of the bended shape film in the reductive solution, led to an acceptable fixation of the temporary shape (74%), while a second oxidation led to a 78% of the recovery shape. Entrapping glucose oxidase enzyme (GOD) in β-CD-CS/Fc-PEI hydrogel by casting technique, made the system glucose-responsive as well. Therefore, the original shape could be recovered in 48 h by direct immersion of the sample in glucose solution (glucose oxidation by GOD led to the formation of hydrogen peroxide, which was the oxidant for the recovery step process).

2.4. Triple and multi-shape SMPs

It is of great interest to develop SMPs with multi-shape properties when complex material movements are required (example of suture wires). In 2005 a double dual-SME was described by Liu et al. They designed a novel kind of poly(methyl methacrylate)-poly(ethylene glycol) (PMMA-PEG) semi-IPN prepared by radical homopolymerization and cross-linking in the presence of linear PEG [60]. Two independent shape-memory behaviors occurred following the melting of PEG crystals and T_g of semi-IPN. Developing SMPs with two different T_{trans}, highlighted an opportunity to widen research and applications. Shortly after, new type of SMPs, the triple-shape memory polymers (t-SMPs) were defined. They were able to change their first temporary shape (A) to a second temporary shape (B) followed by third shape (C) triggered by subsequent temperature increase [61]. One of the first t-SMPs were developed in 2006 by Bellin et al., selecting polymer networks with at least two segregated domains: (1) MACL network made of poly(cyclohexylmethacrylate) (PCHMA) main-chain cross-linked with difunctional PCL, characterized by two T_{trans} (T_m of the polymers) and (2) CLEG network constituted by grafted short PEG side chains on the PCL main chains. The entire system also presented two T_{trans}: one related to T_m of PCL and the other associated to T_g of the CLEG network [62]. In both cases, the permanent domain, giving the original shape (C), was the result of cross-linking reactions. The temporary shapes [(B) and (A)] were successively formed via two-step thermomechanical process, involving the deformation of the materials in their elastic state at temperature higher than the $T_{trans(A\text{ or }B)}$. Physical cross-links determining the (B) shapes were formed by freezing PCHMA domains or by partially crystallizing the PCL segments during cooling under constant load. Second deformation and cooling of the sample led to the production of a new set of physical netpoints related to the crystallization process. Sequential heating allowed the recovery of the first shape

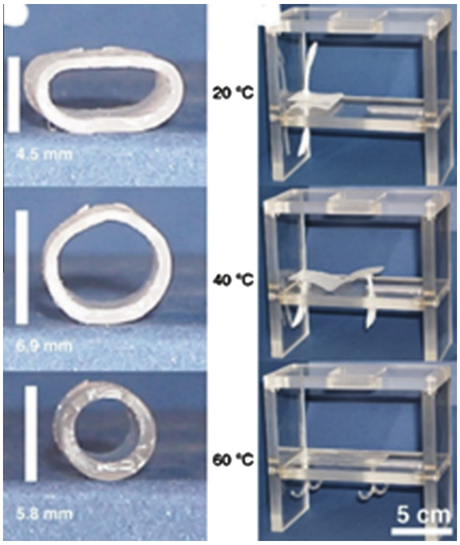

Fig. 4. Shape recovery of tube and plate with anchors based on CLEG networks showing t-SME. Adapted with permission from Bellin et al. [62] copyright 2006 National Academy of Sciences, U.S.A.

(A) and then the shape (C). As presented in Fig. 4, this multi-SME (m-SME) systems could facilitate the design of removable stents or smart fasteners. In an ulterior research, the authors demonstrated that the crystallizable domains of the t-SMP (PCL and PEG phases) can be used for one-step temporary shape fixation applying dual-shape programming process [61]. As a result, MACL networks with triple-shape capability were created using the one-step programming process. The specific network architecture was related to two switchable polymer segments, covalently linked with both chain ends to the polymer network. [63]. Both polymer chain types could be oriented in the same direction by deforming the sample at temperature higher than the T_{trans}, leading to a successive formation of the physical cross-links during the cooling step. Up to date, several t- and/or m-SMPs systems related to two (or more) distinct switching transition domains have been reported [64–74]. In 2009 Xie et al. proposed a new approach in the t-SMP architecture by combining two microscopic phases. They obtained the t-SME through macroscopic bilayer cross-linked polymer structures, where each epoxy layer possessed dual-SME with good R_f and R_r [72]. The phase transitions of each layer were well-separated (38 °C and 75 °C, respectively). Four bilayer epoxy samples with different thickness ratio and strong layer interface were obtained by two-step curing process. To quantify the t-SME a bend temporary shape was used. The fixation of the shapes [(B) and (C)] was strongly correlated to the ratio between the two layers (yielding fixity ratios varying from 70% to 97%). An year later, Luo and co-workers embedded non-woven PCL fibers into a T_g-depending matrix (epoxy-based copolymer thermoset with a T_g from 20 °C to 45 °C) offering well-controlled systems with large degree of flexibility [75]. New trend in the conception of SMPs was proposed using click-chemistry. For example, Zhang et al. used Diels-Alder reactions to produce recyclable PPDO and poly(tetramethylene oxide)co-network with t-SME [67]. Thermo-reversible network obtained between furan- and bismaleimide-end polymer moieties also led to the achievement of recyclable and self-healing materials. Recently, t-SME was observed in systems obtained by self-complementary quadruple hydrogen bonding [64,65]. Xiao et al. developed one step procedure for 2-ureido-4-pyrimidone(UPy)-functionalized PCL/PPDO IPN production via covalent cross-linking (between PPDO and hexamethylene diisocyanate) and self-complementarity hydrogen bonds (between the UPy of the star-shaped PCL) [65]. In the new covalent IPN network, the ability of each polymer segment to achieve crystalline phase was greater compared to the star-shape PCL-PPDO network and the t-SME. Self-complementarity quadruple hydrogen bonding through the UPy-poly(tetramethylene ether)glycol and 4-UPy star-shaped PCL led to the creation of a novel dynamic network showing both t-SME and self-healing properties [64].

Interestingly, t- and m-SMPs can be also designed using one single broad thermal transition. This second approach was first explored by Xie et al., who reported the tunable SME of a commercial perfluorosulfonic acid ionomers (PFSA) [76]. Nafion® is known to display a broad T_g from approximatively 55 °C to 130 °C. The t-SME displayed dual-step programming process at any two sufficiently separated deformation temperatures above the onset of the T_g. Quadruple-SMP (q-SMP) was also described with good recovery ratio but with relatively low degree of fixation of the first two temporary shapes. Compared to the above mentioned strategies, this method presented the advantage to tune the t-SMP without modifying the chemical composition of the polymer. Parallel studies demonstrated the importance of the thermomechanical programming step. It concerned precisely the control of the stress and the strain in the applied methods [77,78]. It was found that this material could memorize the temperature at which the stretching was applied. This means that the recovery of the two shapes happened in the vicinity of the original stretching temperature. This sample behavior was called temperature-memory effect (TME). However, due to the ionomeric nature of Nafion® and poor processability, its implementation in bulky smart devices remains problematic. In contrast thermoplastic amorphous m-SMPs proposed by Luo et al. were easily processable [79]. In this work two comonomers, styrene (St) and methyl acrylate (MA) were used to design V-shaped gradient copolymer by tuning the monomer feeding during living radical copolymerization. Their respective homopolymers have the advantage to possess two well-separate T_g. The observed island morphology, nanodomains of St surrounded by PMMA matrix, confirmed the network structure formation on the basis of the physical cross-linking. The broad T_g of V-shaped poly(St-grad-MA) (ranging from 20 °C to 100 °C), offered the possibility to create various materials with t-, q- and quintuple-SME. Quintuple- and multi-shape memory effect was also described in the literature regarding electrospun membranes based on the thermoplastic polymer Nafion® with broad transition temperature and potential application as smart textiles, artificial intelligence robots, bio-medical engineering [80,81]. Vitrimers are another class of polymers that presented good multi-shape behavior [82]. Finally, a recent work from our group investigated m-SME in miscible polymer pairs with a broad T_g [83]. Indeed, PLLA/PMMA blends processed by twin-screw mini-extruder showed a unique and broad T_g, especially for the 50%/50% blend. This new approach allowed successfully the concept of t-SME using simple process technique.

2.5. SMPs at the origin of future actuators

Based on the described previous progress, another type of shape-memory properties - the two-way shape-memory effect (2W-SME), was actively investigated by the academic research. It has been reported that permanent systems, such as cross-linked semi-crystalline polymers [84–86], nematic liquid-crystalline elastomers [87], and glass-forming polydomain nematic networks [88], open the door to the design of polymeric actuators. There is a significant interest in these polymeric actuators as artificial muscles as well as devices with multiple degree of freedom for endoscopic surgery application.

Generally, the 2W shape-memory phenomenon occurs on both heating and cooling step in the presence or absence of external stress [88]. It was found that reversible chain conformations were responsible for this kind of actuation. Semi-crystalline polymers were one of the easily processed, produced and cross-linked polymers favoring their implementation in the production of cross-linked networks with 2W properties [89]. In 2008 Chung et al. unexpectedly discovered such behavior in poly(cyclooctene) (PCO) films covalently cross-linked by dicumyl peroxide [86]. The 1W-SME of these semi-crystalline thermoset polymers, with T_m easily adjusted by the degree of the cross-linking, was previously reported [90]. Once the working temperature during the cooling step reached the PCO crystallization temperature, a significant increase in strain was observed revealing a potential 2W-SME. In the case when the sample is heated upon constant stress, a tensile contraction of the PCO appeared responsible for the recovery of shape similar to the one observed before crystallization. The observed strain increment was a result of the crystallization process or formation of crystallites oriented along tensile direction upon uniaxial loading. Crystallization induced elongation (CIE) and melting induced contraction (MIC) phenomena were then described in multiphase polymer networks such as star-precursors of polypentadecalactone (PPDL) and PCL [71]. As each crystallizable polyesters segments possess its own CIE and MIC, reversible t-SME was observed since both segments were oriented under constant stretching (Fig. 5). However, the formation of cross-linked networks from semi-crystalline precursors with 2W-SME remained scarcely addressed in the literature because the crystalline features of these segments can be strongly depressed on cross-linking. In this context, in 2011 Raquez et al. reported the production of thermoreversible cross-linked (PCL)-based PUR networks by reactive extrusion technology, which was characterized by 1W- and 2W-shape-memory properties [89]. In our study, the cycloaddition reactions were realized between furan and maleimide moieties, enabling the control of the microstructure. The networks in this case were obtained, by successive reactions between an α,ω-diol PCL, furfuryl alcohol, and methylene diphenyl 4,4′-diisocyanate straightforwardly afforded the α,ω-furfuryl PCL-based PUR systems, and subsequent Diels-Alder reactions with *N,N*-phenylenedimaleimide allowed the synthesis of these thermoreversible cycloadducts. The cross-linking density could be then modulated by partially replacing PCL-diol with PCL-tetraol.

In 2013 Behl et al. have shown that the 2W-SME can be obtained without applying a constant stress for a multiphasic copoly(ester-urethane) network made of, at least, two semi-crystalline polyester segments (PCL and PPDL) [91]. For this purpose, the copoly(ester-urethane) network was first programmed in such a way that the polyester segment with the highest T_m (PPDL) was able to crystallize under a certain stress, followed by the crystallization of the second polyester segment (lower T_m). As PCL was constrained to crystallize towards the chain-extended crystallization process, the copoly(ester-urethane) network can be actuated upon 2W-SME by simply heating and cooling around the PCL T_m without the application of an additional load (Fig. 6).

The same research group developed reversible bidirectional system where the sample actuation upon cooling and heating could be selected by physical manipulation [92]. In this case the strategy was established on the formation of an internal skeleton based on crystallites huddled in nano-clusters acting as physical network and adjusting actuation domains. Covalently cross-linked poly[ethylene-*co*-(vinyl acetate)] (cPEVA), displaying a broad T_m (from 25 °C to 90 °C), allowed the formation of two types of polyethylene (PE) crystallites. One part is associated to the lower T_m range defined as the actuation domain (from $T_{m,onset}$ to intermediate T_m) and the other one was activated by the upper range (from the intermediate T_m to $T_{m,offset}$), so-forming the main skeleton. After macroscopic deformation of the samples at 90 °C ($T_{m,offset}$), the skeleton was achieved under stress after the cooling step ($T_{m,onset}$, 25 °C). Shape (A) was implemented under stress-free conditions by heating the films to the intermediate T_m (50, 65 or 75 °C) and shape (B) was successively obtained by cooling it to 25 °C. Repeatable swapping of the two shapes was demonstrated through application of successive heating/cooling cycles.

Recently, a different approach to actuate the SMPs materials was reported [93]. The strategy consisted in the design of IPN by combining the crystalline component of PCL as switching domain and the elastomer component such as poly

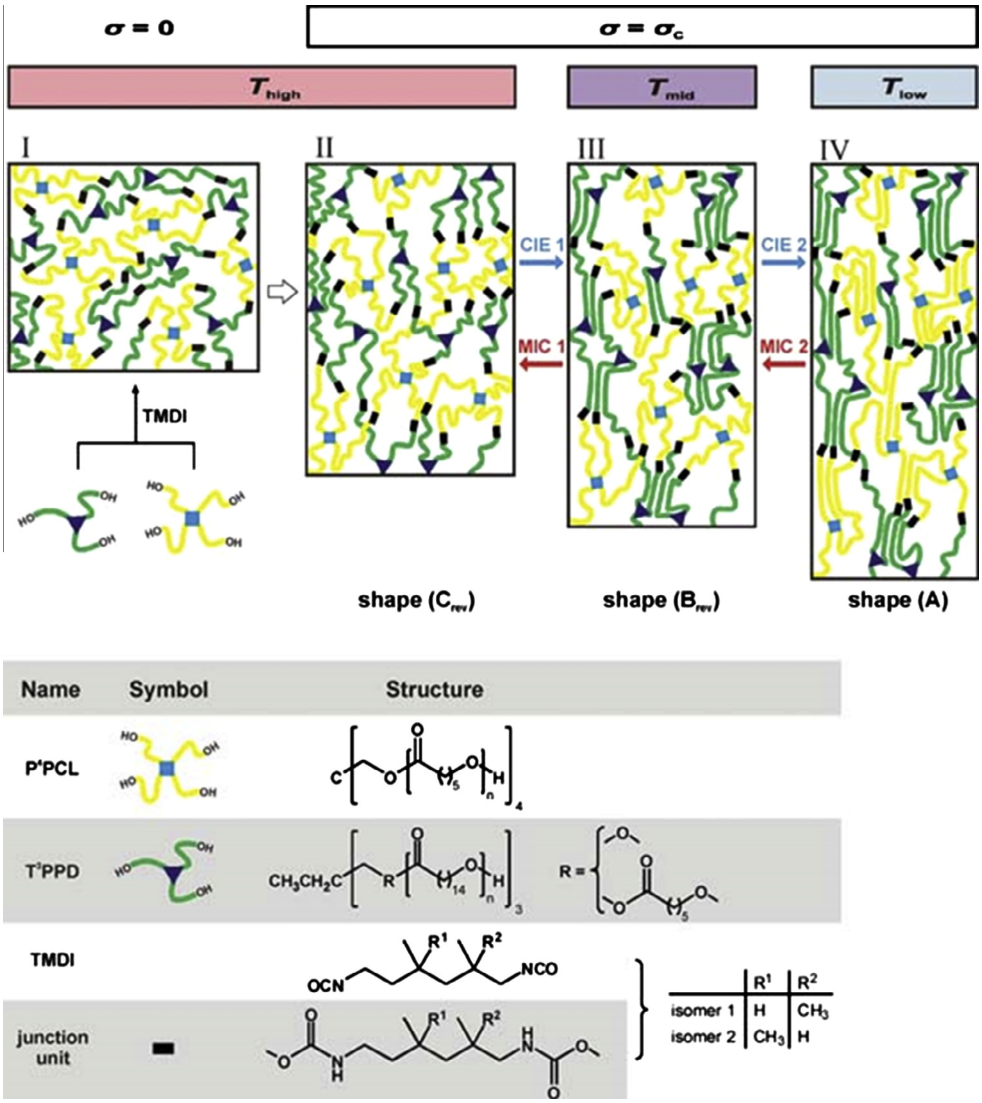

Fig. 5. Reversible t-SME in PCL- and PPDL-based network. Adapted with permission from Zotzmann et al. [71] copyright 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

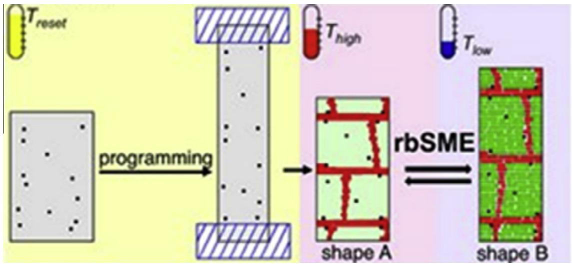

Fig. 6. 2W-actuation of copolymer network made of PCL and PPDL and obtained after skeleton formation. Adapted with permission from Behl et al. [91] copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

(tetramethylene ether)glycol (PTMEG), which acted as a spring. This 2W-shape-memory system presented the advantage to be easy and cheap in addition of its free-loading preparation procedure. In fact, the concept of the IPN required a pre-programming process. Raw materials, including modified macromonomers and cross-linkers, were dissolved in dimethylformamide. Pre-IPN was obtained by photocross-linked of acrylate-PCL. The obtained gel-like structure was then stretched and the final IPN was achieved by curing the PTMEG at 80 °C and subsequent cooling for the formation of the

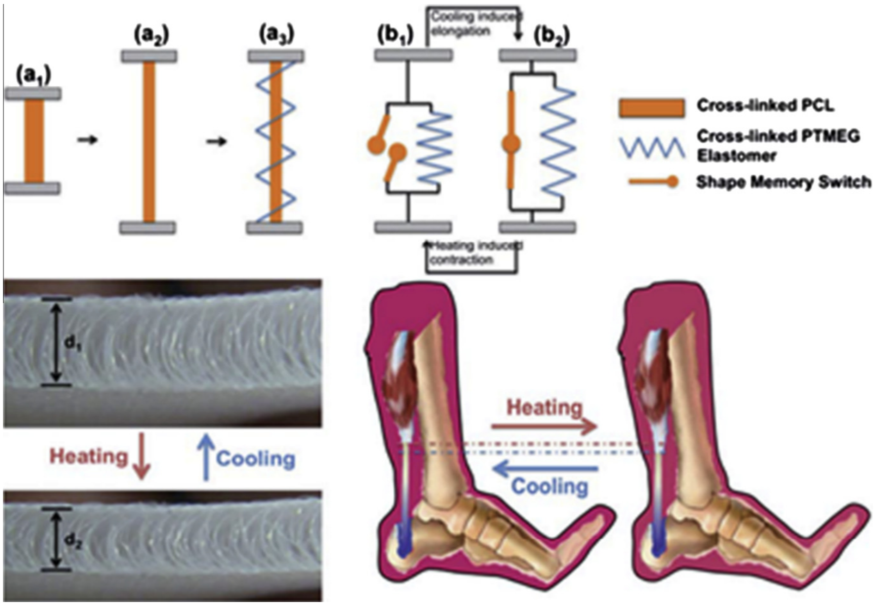

Fig. 7. Elaboration of "switch spring" actuated system and potential applications; a_1 – cross-linked PCL, a_2 – stretched fixed PCL, a_3 – cross-linked PTMEG, b_1 – compressed shape, b_2 – elongated shape. Adapted with permission from Wu et al. [93] copyright 2014 Royal Society of Chemistry.

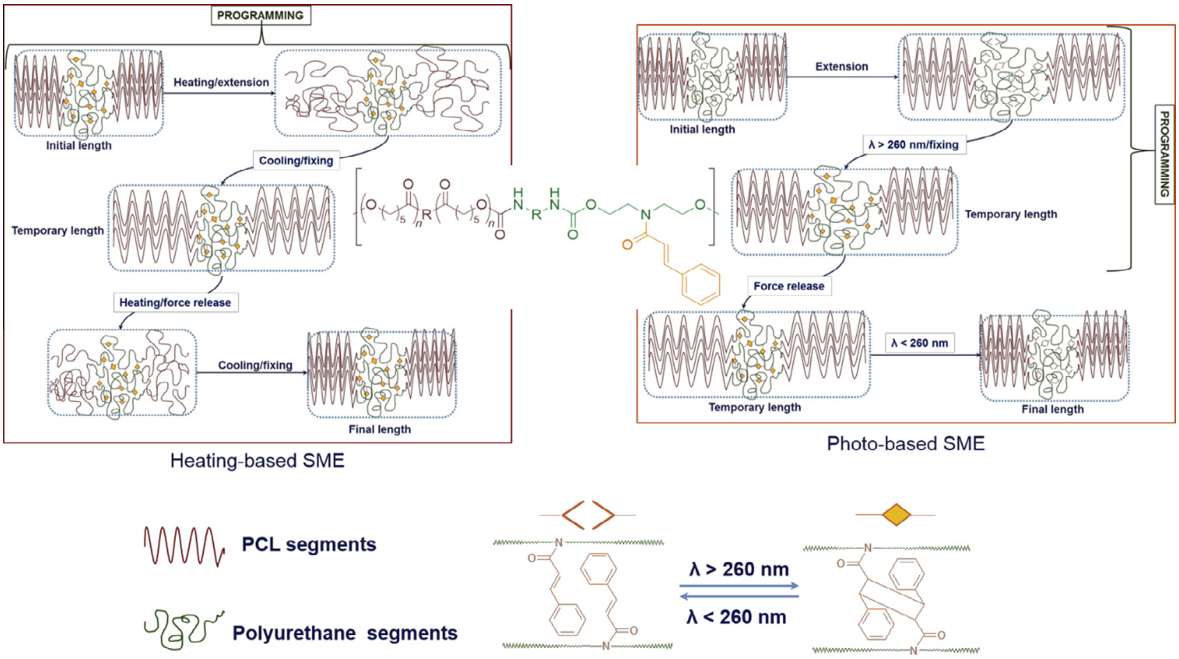

Fig. 8. Thermal and light dual-SME observed in PCL-based PURs. Adapted with permission from Pilate et al. [98] copyright 2014 American Chemical Society.

elastomeric network. Afterwards, by reheating the sample, PCL melted "opening of the switch" and the PTMEG undergone a compression movement. As a consequence, PTMEG pushed the PCL segment to crystallize following "spring direction" when the system was cooled again. Such new tension-free permanent 2W-SMP could be employed as artificial muscles or tendon (Fig. 7).

2.6. Multi-stimuli responsive SMPs

New trends in the polymer devices have been focusing on the development of materials capable of being actuated in response of distinct stimuli via association of different actuation mechanisms. Until now, the multi-stimuli responsive SMPs were one of the less studied systems. Herein, we discussed merely the systems presenting unwanted overlapping effect between the stimuli. New t-SME was obtained by combining UV light irradiation and direct heating in order to fix successively both temporary shapes [94]. In 2013 Wang and co-workers proposed the synthesis of a trifunctional symmetric diester monomer or 4-hydroxycinammic acid (4HCA), which is well-known for its photo-reversibility [95–97]. Further bulk polymerizations with diols (HO-$(CH_2)_n$-OH with n = 2–6) and GeO_2 as catalyst, led to the production of hyperbranched structure by the addition of hydroxy chain-ends to double bond 4HCA units of the polymer backbone. The generated physical cross-links, by chain entanglement, were sufficient on demonstrating the materials thermal- and light-SMEs. The said effect was demonstrated by the bending of the initial shape (A) of the film to a stable round shape (B) via its irradiation upon UV light (λ = 280–450 nm). At the next step, the shape (C) was obtained by hot-deformation at 70 °C of the shape (B). Reheating of the shape (C) at 70 °C gave the photo-active shape (D), the same as the shape (B). Finally it was possible to recover the original shape (A) after 3 h upon UV light irradiation at λ = 250 nm.

In 2014, our research group proposed one of the first dual-stimuli-responsive SMP [98]. The obtained by reactive extrusion technique PURs systems showed independent heating- and photo-based SMEs. They were made of heating responsive PCL containing segments with various degrees of crystallinity and photo-responsive BHECA coupled with an aliphatic diisocyanate. In this case BHECA served as an agent for the formation of the traditional cross-linked network, required for the production of the heating responsive SMPs. It was sufficient to irradiate PUR hot-recovered films at appropriate wavelength to induce [2+2] cycloaddition and form cyclobutane rings and the PCL segments acted as the switching domains by reversible crystallization (Fig. 8). As described in Fig. 8 BHECA could serve itself as a switching segment due to the photo-reactivity of the cinnamoyl moieties. It was found that the PCL degree of crystallinity influenced the shape memory properties of the films upon light irradiation. Both thermal and photo-based SMEs were enhanced by the addition of di- or tetra-cinnamate PCL into the PUR using solvent-casting.

3. Multi-functional SMCs

As already described in the previous section, the most common and convenient way to actuate the SMP materials is a direct increase of the surrounding temperature. However, this exogenous heating is not always suitable for some applications. An alternative way to overcome this problem is to generate direct heat from inside the material. This can be achieved by the incorporation of functional nanofillers into the SMP matrix in order to convert electrical, magnetic, optical, acoustic or chemical energy to heat. Moreover, the production of the SMCs offers the possibility to combine the advantages of polymers and the functional properties of nanofillers. In this purpose, different approaches are discussed concerning the type of loading of the nanostructures into the polymer materials and the subsequent actuation of the devices applying electric current, alternating magnetic field or light as stimulus. The possibility to produce temperature-memory, magnetic field-memory as well as water-sensitive SMPs was also outlined. In each section a special attention was paid to the potential application of the new materials.

3.1. SMCs containing carbon-based nanofillers

Electrically conductive polymeric nanocomposites have been one of the most studied SMPs materials [99]. Their production can be achieved by the incorporation of single-walled carbon nanotubes (CNTs), multi-wall carbon nanotubes (MWCNTs), carbon nanofibers (CNFs), carbon nanopaper, aligned conductive carbon-based nanofillers, carbon black (CB) and graphene. The main role of these nanofillers is to convert the electrical current into heat through Joule effect, so-actuating the SMPs.

Carbon nanotubes are among the most promising reinforcement materials for developing high performance multi-functional nanocomposites [100]. CNTs and MWCNTs both can carry a current density as high as 1×10^9 amp/cm^2 [101]. CNTs also shows great flexibility compared to conventional fiber reinforcements [102]. The concept of electrically conductive SMCs containing (MW)CNTs presents several challenges relating to the good dispersion of the nanofiller in the polymer matrix, interaction with the polymer chains, establishing of electrically conductive network in nanocomposites, etc. These issues have a direct impact on the final mechanical and thermal properties of the materials, thus restricting their application. To overcome the difficulties, several approaches have been developed: (i) direct mixing of the (MW)CNTs with the polymer matrix, (ii) (MW)CNTs surface-modification and blending with the polymer matrix (improvement of the interfacial bonding with the polymer macromolecules), (iii) cross-linking the (MW)CNTs with the polymer matrix, (iv) alignment of the (MW)CNTs in the polymer matrix upon applied electric/magnetic field or (v) conversion of the (MW)CNTs into nanopaper or film and its subsequent incorporation within the polymer matrix [103]. In view of the significant number of published researches on the production of SMPs containing carbon-based nanofillers, we have limited this review to some of the most recent and groundbreaking studies.

Several publications on SMCs concerning the physical blending procedure were already published [104–107]. Traditionally, the direct mixing technique of (MW)CNTs with the polymer matrix led to the formation of aggregates. The lack of functional sites on the conductive nanofillers surface makes difficult their efficient dispersion into the polymer matrix and renders the processing step complex. A good solution on this problem is to use the nanofillers under their macroscopic level features, such as films and yarns. In this context the paper-like (MW)CNTs films (nanopapers) were described as promising

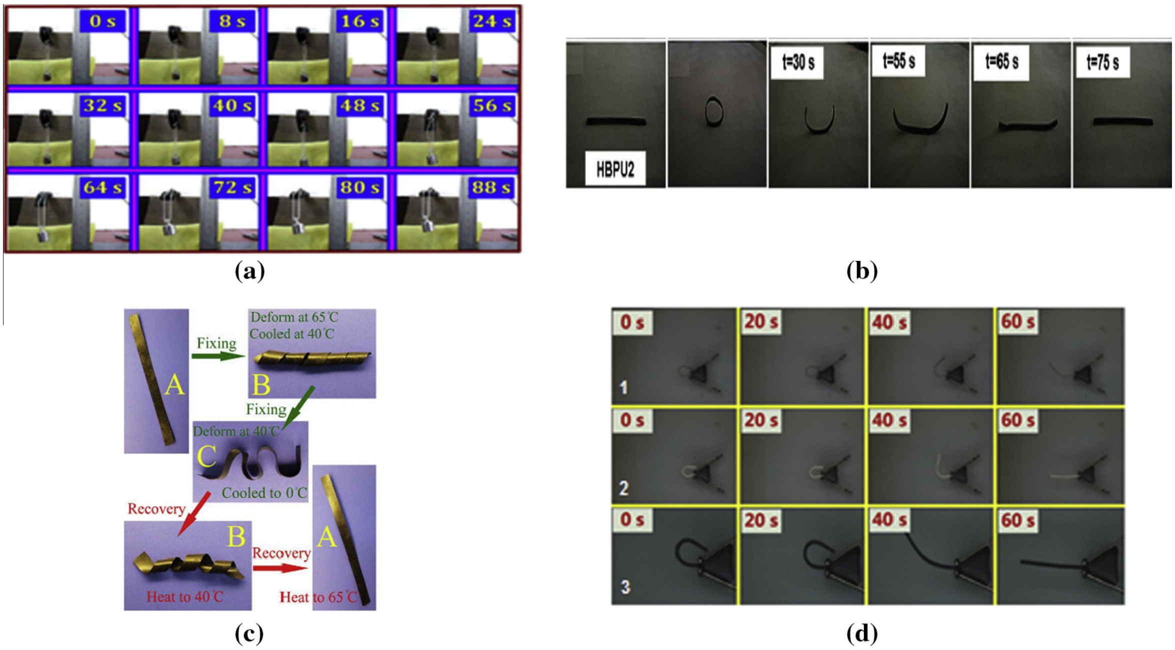

Fig. 9. Electrically actuated SMCs containing (MW)CNTs. Adapted with permission from Lu et al. [111] Crown copyright 2011 Published by Elsevier Ltd. for (a), from Kalita and Karak [116] copyright 2013 Society of Chemical Industry for (b), from Dong et al. [119] copyright 2014 Elsevier Ltd. for (c) and from Lu et al. [123] copyright 2014 Elsevier Ltd for (d).

structures. Generally, they represent self-supporting networks of entangled CNTs in a random fashion and are held together by Van der Waals interactions at the tube-tube junctions. Similar designs are frequently used as fire and lightning strike protection (high current-carrying capability) and electromagnetic shielding interference [108–110]. In the study of Lu et al. three-dimensional self-assembled MWCNTs nanopaper developed onto hydrophilic polycarbonate membrane were synthesized by controlled pressure vacuum deposition procedure [111]. As a result, continuous and compact network with highly conductive property was obtained. The combination of the nanopaper with styrene-based SMP facilitated the actuation of the nanocomposite by electrically resistive heating. Furthermore, the actuating capability of SMCs upon electrical stimulation (35 V) was utilized to drive up a 5-g mass from 0 to 30 mm in height (Fig. 9(a)). It should be noted that the rate of shape recovery is strongly dependent on the magnitude of the applied voltage and the electrical resistivity of the nanocomposite. In addition, the new materials 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. An explanation of this phenomena has been recently proposed by Luo et al. The increase in the resistivity was explained by the enlarged distance between the CNTs in the swelled CNTs-PU bilayer films and the local change in the nanofiller orientation and locations in the material temporary shape [112]. SMP nanopaper with high electrical conductivity and enhanced recovery speed was previously obtained by the self-assembled MWCNTs. The production of the percolating conductive network was possible by the preparation of stable suspension of Triton X-100 (nonionic surfactant) treated MWCNTs [41]. From the reported data, we can envision that this type of nanocomposite can find potential application as sensors, controllable devices, adaptive and deployable structures.

In 2014, Yu et al. demonstrated that microwaves could be another effective stimulus for the actuation of (MW)CNTs loaded styrene containing shape memory resin after direct mixing of the nanofiller [113]. In this case the embedded CNTs, under microwave radiation, absorbed the applied electromagnetic energy and transmitted it into heat generating thermally induced SMCs shape recovery. This wireless remote shape control effect was enhanced with the increasing amount of added CNTs or the irradiation frequency.

Another barely studied effect is the temperature-memory SMCs, where the materials demonstrated the ability to remember the temperature of their deformation. For example in the case of fibrous membranes from poly(vinyl alcohol) (PVA)/CNTs the nanotubes induced a broadening of the T_g and a temperature memory with a peak of recovery stress at the temperature of their initial deformation. Interestingly, the generated stress upon shape recovery was up to two orders of magnitude greater than that one characteristic for the conventional polymers [114].

However, better dispersion of the nanotubes in the polymer matrix can be obtained by their surface chemical modifications. A clear evidence of the positive impact on the SMCs properties was demonstrated by Raja et al. [115]. In this study, nanocomposites of PU and poly(vinylidene difluoride) (PVDF) in presence of pristine or ozone modified MWCNTs were prepared by melt-blending technique. The morphological characterization of the materials revealed better dispersion for the modified conductive nanofillers due to the improved interfacial interaction between the polymer macromolecules and the MWCNTs. The tensile strength and dynamic storage modulus of the SMPs were enhanced compared to the pristine system. In addition, the PU/PVDF films were characterized by better electrical and thermal conductivity. As a result the shape-memory behavior of "U" shaped structures showed 95% recovery of the deformed structure upon constant voltage of 40 V. This effect was faster for the systems containing the modified MWCNTs with recovery time of 15 s compared to the control films where the complete recovery of the films initial shape was of 30 s. SMCs with good performances can be also obtained using triethanolamine functionalized MWCNTs (TEA-f-MWCNTs, MWCNTs up to 2 wt%) [116]. The materials were made of hyperbranched polyurethanes (HPUs) polymer matrix and prepared by *in situ* pre-polymerization technique. As a result of the homogeneous distribution and the strong interfacial interaction of TEA-f-MWCNTs with the PU chains (hydrogen bonding and polar-polar interactions), the nanocomposite presented: significant thermal stability accompanied with increased degree of crystallinity, enhanced tensile strength (28.5 MPa) and scratch resistance (7 kg). The shape recovery rate and shape recovery time was tuned upon microwave irradiation and depended strongly on the source power (Fig. 9(b)). MWCNTs were also modified by direct grafting of L-lactide and oligo(ε-caprolactone) comonomers on their surface and subsequently incorporated in poly(L-lactide-*co*-ε-caprolactone) SMP matrix [117]. Using this method, the nanofillers (2 wt%) were used as an effective physical cross-linking and switching segments in the polymer nanocomposites, ensuring higher SME.

An interesting method to enhance the materials electrical and thermal conductivities is to combine two or more electrically sensitive nanofillers [118]. For this purpose, carboxylic acid-functionalized CNTs were grafted onto the CNFs and then self-assembled by deposition. The synergistic effect of both nanofillers (cross-linked to the epoxy-based matrix), upon Joule heating the shape recovery was observed in 45 s (voltage of 12 V DC and power of 0.5 W). In a very recent study, 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 [119]. In order to achieve this aim, an environmental friendly approach was used. EP-g-TX100 was synthesized and introduced to the CNT-epoxy system as a reactive agent for epoxy emulsion, and a new reversible phase for TSME epoxy structure. The homogenously dispersion of the nanotubes render possible the design of the SMP materials characterized by good mechanical properties as well as two- and triple-shape-memory properties (Fig. 9(c)). The decoration or combination of the (MW)CNTs with metal such as Cu, Fe, Ag and Pt is another promising method to nanoreinforce and electrically actuate the SMCs in a fast manner. These structures were found to be very effective since a small quantity of these nanofillers is necessary to achieve the desirable effect. In this context different studies were already published: Cu-CNT were incorporated in polylactic acid (PLA)/epoxidized soybean oil [120], Fe-MWCNTs and Ag-MWCNTs in PUs [121]. Fe-powder was also used for the production of materials with multi-responsiveness by the deposition of the metal containing layer on one side of the nanocomposites and MWCNTs on the other [106]. The coating of the electrical nanofillers with conductive polymer (polypyrrole-coated MWCNTs) was another effective way to enhance the nanofiller dispersion and the materials mechanical and electrical properties [122].

SMCs with multi-stimuli responsiveness can be obtained by combining CNTs and boron nitride properties [123]. The epoxy-based SMPs were characterized by higher T_g and thermomechanical strength. The embedded CNTs absorbed the light energy and transmitted it into heat to thermally trigger the SME. The boron nitrides improved the thermally conductive property of the films and helped to facilitate the heat transfer from CNTs to the polymer matrix. As presented in Fig. 9(d), the synergistic effect of both nanofillers allowed significantly to improve the SMP IR light-induced shape recovery.

However, in most cases the conductive nanofillers are randomly dispersed in polymer matrices and the resulting polymer materials are characterized by limited mechanical strengths and electrical conductivities. An effective way to enlarge the practical applications of the (MW)CNTs embedded polymer nanocomposites is to assemble the carbon nanotubes into highly aligned structures. The electroactive polymer (EAP) actuators, as new technological devices, are attractive mainly because of their large-strain discontinuous actuations driven by electrical field or current, easily control and low cost [124].

Usually EAP actuators are made of diverse CNTs configurations such as pliable electrodes in order to realize discontinuous and agile movements. Unfortunately, the actuating direction of most polymers cannot be precisely controlled, and the generated low stress and poor stability cannot meet practical applications. An important class of EAPs are the electrothermal actuators (ETAs) because they are of low driving voltage and electrolyte-free. In the study of Li et al. large-area CNT buckypaper (BP, layers of aligned CNT array) as strong and highly anisotropic material was used as a flexible electrode for the production of CNTs loaded double-layer ETA (BP and polydimethylsiloxane layers) [125]. It was demonstrated that it is possible to control the direction and degree of ETAs bending. The materials bent to the BP sides along the length direction of the U-shaped electrodes, and the deformation of the horizontally cut actuator was much larger, with CNTs alignment perpendicular to the U-shaped BP band (Fig. 10(a)). This concept offered the opportunity to create bionic actuation similar in behavior acting to a human-hand (realization of separate and controlled movements for each of the five fingers, Fig. 10(b)). The process reminded very fast (12 s) to achieve the maximum degree of actuation and 28 s to restore the original shapes. Great advantages of such electrolyte-free materials are their low driving voltage (20–200 V) and long service life (over 10,000 times). The materials can find application for the production of flexible, multiform actions or bionic actuations or displays and bionic robots. Bilayer nanocomposite films containing aligned MWCNT/poly[1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene] on isotropic poly(dimethylsiloxane) substrate were previously reported [126]. The SMCs exhibited anisotropic solvent driven reversible bending/unbending actuation (in the bended structure the internal layer is the MWCNTs loaded (Fig. 10(c) and (d)) and the actuating direction in this case was accurately controlled to be perpendicular to the MWCNTs length. What

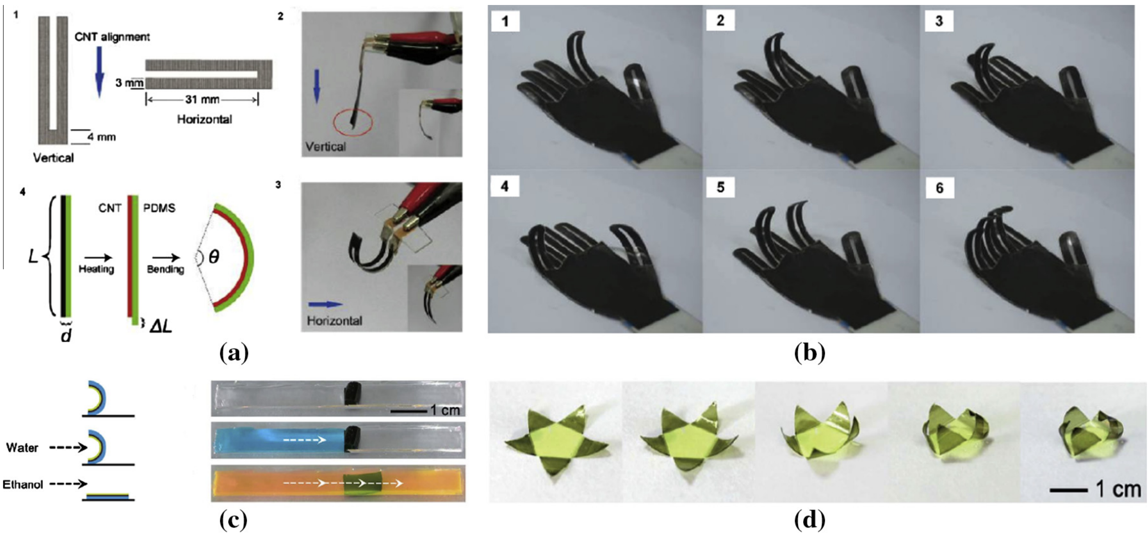

Fig. 10. SMCs bilayer structure containing (a) nanopaper and actuated under electrical current and (b) series of solvent immersion cycles. Adapted with permission from Li et al. [125] copyright 2015 American Chemical Society for (a) and (b) and from Lu et al. [126] copyright 2016 Royal Society of Chemistry for (c) and (d).

is interesting to underline in this case, is that the actuation generated a stress (15 MPa) which was approximately 42 times of the strongest human muscle. Moreover, the reversible actuations were characterized with improved mechanical strength, reported to be repeated for 300 cycles without fatigue. The SMCs structures represented an effective route in the designing of novel high performing artificial muscles.

Similar to CNTs, CNFs possess excellent thermal and electrical conductivities. Generally, for better interfacial bonding they are oxidized and incorporated in the polymer material by direct blending (as nanopaper or hybrid filler of CNF) [127]. This allowed the electrical actuation of the SMCs, which presented enhanced mechanical performance [127–129]. Better dispersion of the CNFs could be achieved by high-power sonication or by *in situ* polymerization and subsequent laminating the CNF papers onto styrene-based SMPs activated upon electric voltage [15,110]. New SMCs with high-speed electrical actuation capability were developed by incorporating continuous, non-woven CNFs into an epoxy SMP matrix [130]. The originality of this system was established on the fiber morphology and their nanoscale dimensions. As a result the conductive network in the SMP was characterized by large interfacial area assuring high electrical conductivity, enhanced heat transfer and recovery stress.

CB is also an effective filler for the reinforcement of the polymer matrix and the maintenance of stable physical cross-linking polymer structure [131]. Often, it is incorporated with another conductive nanofiller. CB was dispersed homogeneously within the polymer matrix and served as interconnections between the carbon fibers, while the fibers acted as long distance charge transporter by forming local conductive paths [132]. This synergistic effect was possible by combining the properties of the CB and the MWCNT nanopaper with nickel nanostrand [133]. The resulting SMCs were characterized by improved electrical and thermal conductivity. In this case the MWCNT nanopaper (laminated on the surface of SMP) served as a continuous path for electric current and the blended magnetic nickel nanostrands improved the thermal conductivity and facilitate the heat transfer from the nanopaper to the SMCs part.

The incorporation of graphene is another method to produce electrically conductive SMCs. In the literature it is described by analogous chemical properties than these of the nanotubes and structure similar with layered nanoclay. Graphene can be incorporated by direct mixing with the polymer matrix for the production of PVA water-induced SMP [134], by its preparation of polymer blends with embedded functionalized graphene (improved interfacial bonding and self-healing materials) [135], by PCL-click coupling with graphene sheet (enhanced mechanical and recovery properties) [136] or by conversion of graphene into paper or film form and incorporation in the polymer matrix [137]. Lu et al. demonstrated that the electrical conductivity of the graphene-based polymer materials can be improved at low voltage by the incorporation self-assembled and grafted graphene oxide onto the carbon fibers [138,139]. The synergistic effect of both nanofillers enhanced the reliability in bonding between carbon fiber and SMP matrix via Van der Waals and covalent cross-links, respectively.

3.2. SMCs containing noble metals

Nanosized noble metal structures such as silver (Ag) and gold (Au) nanoparticles (NPs), nanorods (NRs), nanowhiskers (NWs) and nanowires (NWrs) are of great interest for the production of new generation multi-responsive SMCs. Their large specific surface and strong surface plasmonic resonance (SPR) properties, offered the structures property to absorb specific

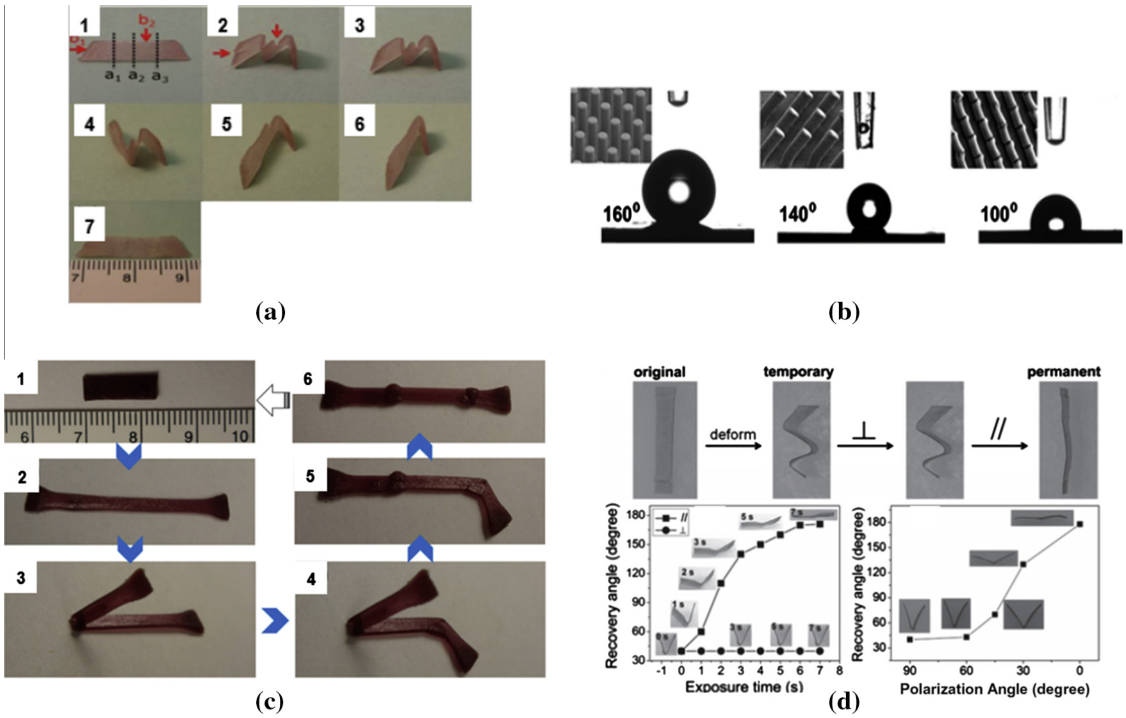

Fig. 11. SMCs materials containing Au nanofillers. Adapted with permission from Zhang and Zhao [140] copyright 2013 American chemical society for (a), from Zheng et al. [143] copyright 2015 The royal society of chemistry for (b), from Zhang et al. [39] copyright 2014 American chemical society for (c) and from Zhang et al. [145] copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim for (d).

wavelength in the range from deep UV to near IR light and to convert it to heat energy (photo-thermal effect). This presented the possibility to produce SMP materials with proper wavelength activation and local shape actuation.

3.2.1. SMCs containing gold nanofillers

In 2013, Zhang et al. demonstrated that Au NPs can be used not only for the observation of optically controllable SME but also to confer self-healing properties (SHP) to the polymer materials [140]. A great challenge in this kind of materials is that SMPs require a permanent network structure (typically chemically cross-linking) which is in conflict with the high chain mobility and interdiffusion needed for the production of SHP. In this point for the design of the SHP it is preferable to produce materials on one single-polymer with both light-controlled shape-memory and optical healing capabilities. The incorporation of small amount of poly(ethylene glycol)methyl ether functionalized Au NPs (0.003 wt%) to cross-linked poly (ethylene oxide) (PEO) films was sufficient to confer such properties to the films. Moreover, after the incorporation of the nanofillers, in the polymer materials it was possible to assure their photo-thermally induced healable and SME properties. Digital images of the self-healing and the light-induced shape recovery process of the produced systems are presented in Fig. 11(a). Even more, the obtained materials were characterized by mechanical properties close to these of the same material before cracking.

Light-sensitive biocompatible polymer networks-based on poly(β-amino esters) containing Au NRs have been recently developed [141]. The produced nanocomposites presented SME upon local irradiation with IR light and subsequent heating above the polymer T_g. As a result, an instantaneous shape recovery was observed until this change moved the sample outside of the beam's path. The authors demonstrated that the thermal transitions of the networks (from glassy to rubbery) can be tuned through the cross-linked density and the introduction of the NRs. Moreover the materials were not toxic against cells and had mild inflammatory response. Therefore Hribar et al. produced biocompatible polymer-Au NRs nanocomposites (films and microspheres) for the release of an antitumor agent doxorubicin. The obtained poly(β-amino ester)-based materials were designed for IR light-responsive with a T_g close to the temperature of the human body and exhibited enhanced therapeutic efficacy in terms of limiting the proliferation of tumor T6-17 cells [142]. From on the published research it is clear that the near-IR light-sensitive SMP materials can find wide biomedical application since this irradiation can penetrate the body tissue.

New horizons of application for the functional and actuated SMPs are light-guided smart windows, light-tracking solar panels, actuators, dry adhesives, etc. Zheng et al. described the production of light-responsive SMP micropillar arrays containing PEGylated Au NRs (up to 0.2 mol%) by replica molding from a poly(dimethylsiloxane) mold [143]. In order to obtain the temporary shape of the microstructures, the materials were bent by exercising a load on top of the sample and this above its T_g. The deformed structure was locked after cooling down the sample to room temperature. Upon laser irradiation (wavelength of 532 nm; power of 0.3 W) the pillars presented local actuation by recovering their initial shape in 5 s. This phenomenon was accompanied by a switch of optical properties of the films - from opaque (bent pillars) to transparent (straight pillars) and *vice versa*. This experiment proved that the change in the films surface topography (bent of straight position of the micropillars) has a direct impact on the materials wetting and hydrophobic properties (Fig. 11(b)). Epoxy-based SMP pillars covered with a thin film of Au or Au-palladium alloy (thickness of 20 nm) were also reported ensuring the material unidirectional wetting properties. An anisotropic liquid spreading behavior was recorded where the water droplets propagated in direction opposite to the pillar tilting [144]. Cross-linked PEO loaded matrix with a small amount of Au NPs (0.5 wt%) demonstrated controlled SPR absorption of the nanofillers and allowed the formation of a temperature gradient in the temporary shape of the polymer resulting in anisotropic polymer chain relaxation and strain energy release [39]. As a consequence it was possible to create a multitude of deformations and to control the mechanical motions of the SMCs (Fig. 11(c)). Variation of the light polarization can also be used as an effective way to control the photo-thermal effect [145]. For this purpose PVA/AuNRs (nanofillers of 0.02 wt%) films were stretching above the polymer T_g and cooled to ambient temperature. In reference to this data, the NRs were oriented in the materials and their light absorption spectrum became light polarization dependent. The shape-memory behavior of material was easily controlled using the light polarization direction, the time of exposure and the polarization angle (Fig. 11(d)).

3.2.2. SMCs containing silver nanofillers

Promising method for the production of SMPs with physical cross-linking structures is the use of metal-ligand coordination systems. Wang et al. described SMCs containing Ag (Ag, 3 wt%)-coordination polymer network [146]. In this case the polymer matrix was isonicotinate-functionalized polyester (PIE) and the pyrazinamide groups were located in the polymer side chains representing the ligand for the Ag ions. It was reported that the degree of cross-linking of the polymer network and the recovery of the initial shape can be easily modulated by the amount of the absorbed ions. As a consequence the addition of the metal ions led to an increase of the film rigidity (higher storage modulus of 1130 MPa) compared to the pristine films (950 MPa). The produced SMP also acted as a reservoir of the metal ions, allowing their release once the polymer network was placed in physiological conditions. The films exhibited antibacterial properties against *Escherichia coli* and good cytocompatibility with osteoblast cells favoring their biomedical application as smart medical devices (wound dressings, implants, etc.). Schematic presentation of the films architecture, SME and their antibacterial effect are summarized in Fig. 12(a).

Ag NWrs are other interesting structures for their high thermal and electrical conductivity. They offer the possibility to produce metallic nanotubes, stretchable and transparent conducting electrodes and semiconductors, organic light-emitting diodes, organic solar cells, touch screens, electrochemical devices, capacities sensor, etc. [147]. A critical issue for their production is the homogeneous dispersion of the Ag NWrs and the construction of conductive percolating network. New tendency in the designing of SMCs is the fabrication of bi- or multilayer structures instead of direct blending of the nanofillers with the polymers. Recently, bilayer films were reported, where one of the layer contained Ag NWrs and the other was SMPUs [148,149]. Schematic representation of the films concept is shown in Fig. 12(b). In these studies it was shown that the bilayer materials were flexible and highly conductive: the application of 1.5 V (DC voltage) was sufficient to turn on the LED. On the other hand, the electrical properties were strain-dependent. The materials conductivity was preserved as the films elongation was less than 12% and their resistance significantly increased (200 Ω/sq). The Ag NWrs-SMPU exhibited good and fast electro-responsive shape recovery as a consequence of the Joule effect heating (Fig. 12(b)). For greater stretching of the films, a loss of conductivity was observed due to the increase in the length of the conductive path and difficulties in the electrons transfer. The described results demonstrated that the Ag NWrs-based nanocomposites can find potential application in the production of wearable flexible and conductive electronics with multi-functional SMPs.

Deformable electronic devices are desired for many new applications, such as wearable displays, solar panels, and non-invasive biomedical devices, where large deformation may be encountered to cope with body movements. Highly flexible SMP bilayer electrodes containing Ag NWrs (diameter of 60 nm and length of 6 μm) can be successfully used for potential elaboration of polymer light-emitting diodes [150]. By a simple two-step procedure, bilayer films of layer Ag NWrs and cross-linked polyacrylate layer were created. The materials have the advantage of being transparent with smooth surface (roughness less than 5 nm) preventing the shocks across the semiconductor films. Moreover the shape-memory properties of the cross-linked network allowed the repeatedly programming of the materials: under compressive strain (bent up to 16% without significant change in sheet resistance) or upon tensile strain (accompanied by a slight increase in the sheet resistance). After the recovery step, the resistance change was fully reserved and a minimal loss of the materials electroluminescent property was registered. The efficacy of the produced Ag NWrs/polyacrylate electrodes of 14 cd/A was found to be slightly higher than the usually used indium-doped tin oxide (ITO) anode.

The application of Ag embedded SMCs in the field of flexible solar modules (polymer solar cells of semi-transparent solar cells in windows) is of great interest since they involve low-cost solar energy, great materials choice and manufacturing advantages [151]. An important parameter influencing the materials properties is the nanofiller morphology. In the study of Yu et al. a special attention was paid on the Ag NWrs length [152]. Short Ag NWrs (length of 4–10 μm) led to the production of devices with high fill factor (FF) as a consequence of the high surface coverage of the nanowires, but with a low photo-current due to the loss of transmittance. In contrast, using long Ag NWrs (length above 20 μm) the devices had high photo-current but lower FF. SMC containing a stack of short and long NWrs (high photo-current and FF) possessed

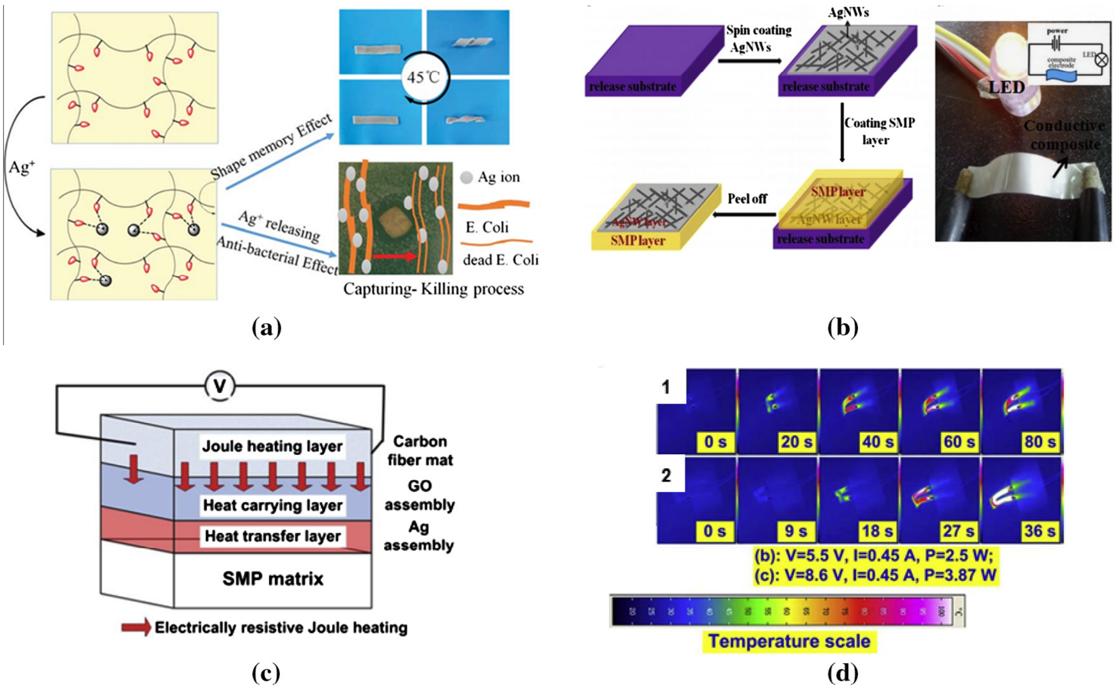

Fig. 12. SMCs materials containing Ag nanofillers. Adapted with permission from Wang et al. [146] copyright 2014 The Royal Society of Chemistry for (a), from Luo et al. [149] copyright 2014 Elsevier B.V. for (b) and from Lu et al. [154] copyright 2014 Wiley Periodicals, Inc. for (c) and (d).

around 3.3% power conversion efficiency which is similar to control devices on ITO/glass substrates. The produced Ag NWrs-polymethacrylate nanocomposite electrodes were defined as highly flexible and could be bent to a maximum 8% tensile strain.

Multilayer SMCs can be produced through the combination of different nanofillers. Several studies dealing with this concept have already been published [153,154]. In order to improve the electro-thermal properties and electro-activated shape-recovery performance of epoxy-based thermoset SMP resin, the Ag NPs - decorated graphene oxide (GO) assembly grafted onto carbon fibers were used. In the obtained multilayer nanocomposite, the carbon fibers were used to achieve Joule-heating induced shape recovery of the materials. The self-assembled GO grafted onto the carbon fibers acted as a Joule-heat-carrying layer (because of their excellent electrical and thermal conductivities) and the silver-nanoparticle-decorated GO was used to decrease the thermal dissimilarity and facilitate heat-transfer from the carbon fiber to the polymer matrix. Schematic presentation of the SMCs architecture is shown in Fig. 12(c). The coating of the carbon fiber mat grafted with Ag NPs-decorated GO onto the surface of SMP was realized via resin-transfer molding. With such a design, it was possible to modulate the electrical resistivity of the multilayer films by varying the GO and Ag NPs content. The bend n-like shape (temporary shape) materials were successfully actuated after the application of direct-current electric field of 8.6 V. The recovery to the initial shape was achieved above the polymer T_g and it was dependent on the magnitude of the applied voltage and the electrical properties of the SMCs. As presented in Fig. 12(d-2), this process was faster for nanofiller containing films (36 s). These results demonstrated that the Ag NPs enhanced the uniform heat transfer in the nanocomposites which resulted in faster shape recovery.

3.3. SMCs containing metal oxide nanofillers

Magnetically addressable SMPs present an attractive application where magnetic nanofillers take part of the materials building block. In these systems, the magnetic NPs play the role of inductive heaters, which offer the possibility to remotely trigger the change between two or more discrete shapes of an object via the application of an alternating magnetic field [155]. Such an approach was found to be of interest for the production of devices for biomedical applications where it is possible to realize a noncontact harmless activation of an object within the body without heating the tissue [156]. One of the most commonly used magnetically sensitive nanofillers are the iron oxides (Fe_3O_4) NPs. These are characterized with good biocompatibility, nontoxicity and high magnetism, thus making them suitable for the design of magnetic drug targeting systems, magnetic resonance imaging for clinical diagnosis, recording materials catalysts, magnetically controlled smart implants, etc.

The traditional approach for the creation of magnetic SMPs is by physical incorporation of the Fe_3O_4 NPs into an SMP, where no specific interaction is taking place between the nanofiller and the polymer matrix. For better dispersion of the

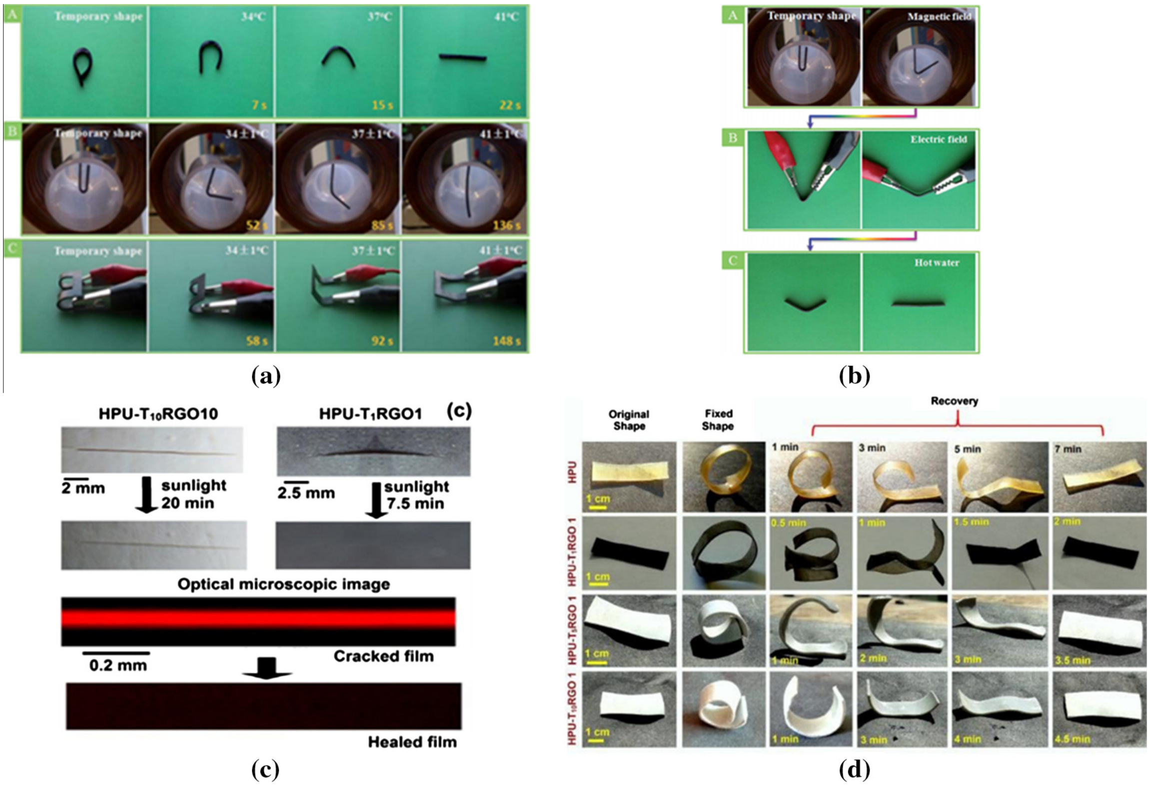

Fig. 13. SMCs materials containing Fe_3O_4 and TiO_2 NPs as nanofillers. Cross-linked PCL SMPs containing Fe_3O_4 decorated with conductive MWCNTs actuated under thermal, magnetic and electrical stimulus (a) and (b) and HPU SMCs materials loaded with TiO_2 NPs with self-healing (c) and shape recovery properties (d). Adapted with permission from Li et al. [166] copyright 2014 Royal society of chemistry for (a) and (b) and from Thakur and Karak [172] copyright Royal Society of Chemistry 2016 for (c) and (d).

nanostructures, the surface is somewhat (non)covalently modified in order to enhance their miscibility within the material and create nanoscale netpoints in the polymer matrix. For example, Fe_3O_4 NPs obtained by co-precipitation of divalent and trivalent iron salts using PEG-10000 as a dispersing surfactant were uniformly dispersed in the biocompatible poly(D,L-lactide) (PDLLA/Fe_3O_4 weight ratios of 1:1, 2:1, 3:1). The materials presented enhanced tensile properties were explained the occurred interaction between the NPs and the PDLLA (hydrogen bonding between Fe-OH group of Fe_3O_4 and O=C of PDLLA) and SME upon alternating magnetic field (frequency of 20 kHz and strength of 6.8 kA/m). The recovery ratio in this system was depending on the physical entanglements of molecular chains and the NPs content (average specimen response time around 35 s) [157]. Fe_3O_4 NPs initially synthesized by co-precipitation method followed by their surface modification using oleic acid were incorporated in PLLA. The evenly dispersed nanofiller (up to 20 wt%) led to an improvement of the mechanical properties of the materials (elastic modulus, tensile strength and elongation at break) as well as their shape-memory properties. Higher Fe_3O_4 NPs content (30 or 40 wt%) led to a deterioration of these properties as a result of the NPs agglomeration inside the polymer matrix. However, the shape recovery ratio in PLLA/Fe_3O_4 (nanofiller content 10 wt %) and the recovery speed in an alternating magnetic field are lower than that occurred in water at 70 °C (Fig. 13(a)). In this case the authors attributed the lower shape recovery ratio and the recovery speed to the low frequency and strength of the magnetic field, which lead to the small heat generated by the Fe_3O_4 NPs [158]. PCL as a semi-crystalline and biocompatible polymer is another suitable candidate for the production of magnetically responsive materials. In the literature linear cross-linked PCL thermo- and magnetic sensitive materials were reported [159,160]. Of interest was the materials degree of degradation, which was accelerated with the addition of the Fe_3O_4. This effect was explained by the hydrophilic nature of the NPs promoting the hydrolysis of the polymer ester bonds. As a consequence SMP permanent domain was damaged and the SME performance decreased. This study demonstrated that hydrophilic nanofillers could be used indirectly as modulating agent for the SMP degree of degradation constructing implants with desired life time, function and shape-memory properties. Other suitable candidates for the production of magnetic NPs (up to 10 wt%) loaded SMPs are the HPUs [161,162]. They present the advantage of possessing low viscosity, high solubility and reactivity, and good compatibilizing capacity. The obtained materials were non-contact activated under microwave stimulus and were characterized by improved mechanical and thermal properties. In 2014 Bai et al. developed a one-pot synthesis of norbornene-capped super-paramagnetic iron oxide NPs and their integration into polynorbornene by ring-opening metathesis polymerization of norbornene in the presence of the NPs [163]. Exploring this idea, it was possible to produce new magnetically addressable SMPs in which the Fe_3O_4

NPs (up to 20 wt%) were well dispersed and interacted via specific non-covalent complexation with the carboxylate moieties of the polymer. The functionalized NPs acted as cross-links and magnetic-induction heaters in the macromolecular network architecture where the polymer was in amorphous state. The nanocomposites were characterized by a superparamagnetic response, with saturation magnetization of around 2 and 5 emu/g for the nanocomposites with 10 and 20 wt% Fe_3O_4, respectively. The reversible nature of the non-covalent binding of the polymerizable ligands to the Fe_3O_4 nanoparticles was strong enough to bestow the materials with the ability to form appropriately strong networks that exhibit shape-memory behavior. Those depended on the NPs content: better results for the lower Fe_3O_4 containing materials (up to 1 wt%).

In the study of Shuang et al., vinyl-capped Fe_3O_4 NPs was used as an effective cross-linking agent for the preparation of the polyPMMA-PEG SMP materials [164]. The new molecular design ensured the good distribution of the NPs, prevented their displacement and reaggregation in the polymer matrix. Apart from the enhanced mechanical properties the materials showed uniform heat-generation and heat-transfer in alternating magnetic field environment. Therefore, the systems presented durable shape-memory performance during the programmed deformation-recovery processes. Moreover, the novel remote-activated SMP exhibited faster magnetic responsiveness compared to the SMPs with physically dispersed NPs and good stability when exposed at high temperature and external stress are applied. Homogenous dispersion and enhanced compatibility of the nanofiller within the polymer matrix could be also achieved by grafting oligomers on the NPs surface. For instance, Schmidt et al. incorporated oligo(ε-caprolactone)-grafted Fe_3O_4 superparamagnetic NPs into thermosets of oligo(ε-caprolactone)dimethacrylate/butyl acrylate [165]. It was shown that the biocompatible material recovered its original straight shape in 20 s when magnetic field with frequency of 300 kHz and power of 5.0 kW are applied.

In 2014, Li and co-workers demonstrated that it was possible to obtain a novel type of SMCs using biodegradable and biocompatible chemically cross-linked PCL with allyl alcohol as polymer matrix and Fe_3O_4 decorated conductive MWCNTs (Fe_3O_4@M) as a magnetism and electricity responsive source [166]. The Fe_3O_4 NPs (diameter of 20 nm) were fabricated by chemical coprecipitation of Fe^{3+} and Fe^{2+} ions on the surface of the carboxyl-modified MWCNTs (diameter of 20–30 nm and a length of 20–30 mm). The advantage here was that the magnetic Fe_3O_4 layer covered the outside of the MWCNTs and contributed to the magnetic properties while the outside of the WMCNTs (without NPs loading) were responsible for the electric properties of the material. The incorporation of the nanofillers with different properties offered the possibility to produce multi-stimuli responsive SMPs upon external thermal (hot water), magnetic field (frequency of 20 kHz and strength of 6.8 kA/m) and electric field (60 V) stimuli (Fig. 13(a)). Moreover, it was demonstrated that the nanocomposite exhibited multistage stimulus recovery from a temporary shape to a permanent one, triggered by alternating the stimuli and this was close to the human physiological temperature (Fig. 13(b)). Due to the semi-crystalline nature of the polymer, the materials also exhibited 2W-reversible shape-memory capabilities when subjected to a constant load during heating and cooling on a thermal region ranging from above T_m to below the crystallization temperature. The Fe_3O_4@M-filled materials had good biocompatibility against osteoblast cells, suggesting their potential application as smart medical devices (implants, functional tissue engineering constructs and artificial muscles). Biocompatible multi-stimuli responsive SMCs were also obtained using poly(ε-caprolactone)-PU as a polymer matrix [167]. The Fe_3O_4 loaded materials (10 or 30 wt%) recovered their initial shape in temperature range close to the human body (hot water response) and when placed in alternating magnetic field (f of 45 kHz and H up to 35.7 kA/m), which made them suitable for sensitive biomedical devices.

Fe_3O_4 in SMPs could be used not only as nanoreinforced agent as well as an effective nanofiller for the generation of gradual hydrolysis degradation of sunflower oil modified HPU/Fe_3O_4 materials [168]. Moreover, the biocompatible nanocomposites (Fe_3O_4 content of 15 wt%) exhibited excellent antimicrobial activity, prevented the biofilm formation against *Staphylococcus aureus* and *Klebsiella pneumoniae* and had a good cytocompatibility with different cells lines. Based on the obtained results the materials were classified as suitable for biomedical applications (magnetically controlled smart implants and tissue engineering scaffolds).

Semiconductor photo-catalysts, such as TiO_2 NPs, are another metal oxide nanofillers used for the nanoreinforcement of the SMCs. They are characterized by large specific surface area and possess remarkable photo-catalytic properties especially, photo-stability in solution, nontoxicity, redox selectivity and strong oxidizing power. Currently TiO_2 NPs are used for wastewater treatment, preparation of photo-induced hydrophilic coatings and self-cleaning devices. This makes them an interesting candidate for the production of materials with SHP or for application in minimally invasive surgery [169].

Until now few studies have focused on SMCs containing TiO_2 NPs. Iijima et al. discussed the surface-modification of the nanofillers with anionic surfactant [170]. The structure presented anionic head group and organic chains that branched into a hydrophobic alkyl and a hydrophilic PEG chain ended by a polymerizable vinyl group. As a result of the surfactant complex properties, TiO_2 NPs were completely dispersed in various organic solvents (alcohols, nitriles, ketones and acetates) and polymers [epoxy resin and poly(methylmethacrylate) resin]. The obtained TiO_2/epoxy nanocomposites possessed shape-memory properties by recovering under direct heating its initial shape. The concept of biodegradable SMPs containing TiO_2 NPs was also reported in the literature [171]. For this purpose the metal oxide was surface-modified by ring-opening polymerization of ε-caprolactone (*g*-TiO_2) ensuring its good dispersion in the poly(L-lactide-*co*-ε-caprolactone) (PLCL) polymer matrix. Due to the additional physical cross-linking between the polymer chains of *g*-TiO_2 and PLCL the obtained nanocomposites (TiO_2 of 5 wt%) presented enhanced mechanical properties: increase of the tensile strength and of the elongation at break, and shape-memory properties compared to these of the PLCL films.

Great challenge in the SMCs chemical architecture is the production of multi-functional materials. In a recently published study, HPU films with shape-memory, SHP and self-cleaning properties (SCP) upon sunlight exposure were reported [172].

This was achieved by the combination of TiO_2 NPs and reduced graphene oxide (RGO, RGO up to 1 wt%). Consequently, simple modulation of the nanofillers amount and composition allowed to tune the materials properties. Digital and optical microscopic photographs of cracked and healed nanocomposite films are presented in Fig. 13(c). On the other hand high amount of TiO_2 NPs (5–10 wt%) conferred good SCP by photocatalytic degradation (within 2–3 h) of a model dye - methylene blue. Moreover, it was shown that under sunlight exposure the SMC presented rapid and greater shape recovery (R_r 91–95%) in comparison to the pristine HPU materials. This was explained with the high light absorbing capacity of RGO and its energy transfer allowing the heating of the sample at temperature close to the polymer T_m (Fig. 13(d)). The mechanical properties of the materials were also nanofiller-dose depended. Due to the hyperbranched structure of the polymer, the HPU films were characterized by poor mechanical properties. In contrast, all HPU nanocomposites possessed significantly improved tensile strength, tensile modulus, toughness and elongation at break. The nanoreinforced phenomena was explained by the good dispersion of nanohybrid, its compatibility and interfacial interactions with the polymer chains (higher aspect ratio of RGO and presence of hydroxyl groups and polar Ti-O groups).

Zinc oxide (ZnO) possess unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photo-stability. The piezo- and pyroelectric properties of this filler allow its use as a sensor, converter, energy generator and photocatalyst in hydrogen production. Because of its hardness, rigidity and piezoelectric constant it is an important material in the ceramics industry, while its low toxicity, biocompatibility and biodegradability make it a material of interest for biomedical application [173]. In the literature, there are few articles on the ZnO SMCs loading. They are containing imidazole-zinc ion for the production of coordinated shape-memory hydrogel [174], triple-shape-memory poly(acrylonitrile 2-methacryloyloxyethyl phosphorylcholine) from dipole–dipole-zinc ion coordination [175] or epoxy-based SMP containing metallosupramolecular unit formed by coordinating 2,6-bis(*N*-methyl-benzimidazolyl)-pyridine ligands to zinc di[bis(trifluoromethylsulfonyl)-imide] [176], ZnO NRs in PU matrix [177,178].

3.4. SMCs containing cellulose nanocrystals

Characterized with their renewable resources, stiffness, and biocompatibility cellulose nanocrystals (CNCs, previously known as cellulose nanowhiskers) have been considered as a suitable nanoreinforcing material for divers biopolymers [179]. Furthermore, CNCs are derived from the most abundant biopolymers and offer many advantages, such as low cost, low density, availability, renewability and unsurpassed quintessential physical and chemical properties [180]. Their chemical structure (presence of hydroxyl groups) offers the possibility to form high-modulus and interconnected CNCs network in the polymer matrix via hydrogen bonding. An advantage of this nanofiller is that they exhibit high stiffness and high aspect ratio [181]. Generally CNCs are defined with low toxicity, which makes them attractive for the production of water-induced SMCs with potential biomedical applications (self-tightening sutures and self-retractable and removable vascular stents). However, the preparation of nanocomposites by direct physical incorporation of CNCs into the polymeric matrix is quite difficult due to the poor affinity between the nanofillers and the polymer chains leading to an insignificant increase in or even failure to improve the mechanical properties of the polymer. Liu et al. described an interesting approach for the production of thermos-responsive and water-responsive SMCs by using CNCs as a cross-linking agent [182]. The network was obtained by chemically bonded the CNCs via their hydroxyl groups to low molecular 4,4-diphenylmethane diisocyanate end-functionalized PCL and PEG. The PEG[60]-PCL[40]-CNC[10] biocompatible nanocomposite exhibited excellent thermo-induced and water-induced shape-memory effects (temperature range close to the human body temperature) as presented in Fig. 14(a) and (b). In both cases, the R_r was around 85% and the materials shape-memory properties depended on the polymer degree of crystallinity and the materials degree of cross-linking. For the water responsive case the films presented a certain degree of swelling, which was directly related to their biodegradability.

On the other hand the strategy to cross-link CNCs with low molecular weight PEG and PCL was proven to be effective for the enhancement of the materials' mechanical strength by variation of the PEG content and the incorporation of the nanocrystals (tensile stress of 6.28 MPa and elongation to break of 160% for PEG[60]–PCL[40]–CNC[10], CNCs of 10 wt%). Another great advantage of this system was its good hydrophilicity (presence of CNCs and PEG), biocompatibility of all used components, controllable biodegradability as well as good cytocompatibility against osteoblast cells. This makes them suitable for the design of new smart biomaterials such as self-tightening sutures and self-retractable smart stents.

It is worth mentioning that CNCs offer a possibility to produce water-sensitive SMPs whose triggering mechanism is completely athermal compared to the traditional systems where water (or other solvent) is used as plasticizers in order to lower T_g of polymer and leading to the materials shape recovery at room temperature or lower. Water-activated mechanically adaptive PU SMPCs containing CNCs have also been described in the literature [183]. In their dry state the materials possessed enhanced mechanical properties (nanofiller content above the percolation limit) and upon deionized water exposure they swelled slightly. This effect allowed the materials water-induced shape recovery and led to a decrease in the storage modulus values due to the competitive hydrogen bonding between water molecules and the nanofillers or the nanowhiskers-rubbery matrix network. In this mind, in 2012 Zhu et al. reported novel and effective strategy to design elastomeric thermoplastic PU/CNCs materials with rapidly switchable shape recovery (10 min) [184]. The sample water triggering in this case was made on the successful combination of the nanofiller percolation network chemo-mechanical adaptability and the entropic elasticity of the elastomer. Such water-responsive materials are promising for the production of breathable clothing and medical devices triggered by human body liquids. Water-active shape-memory materials using

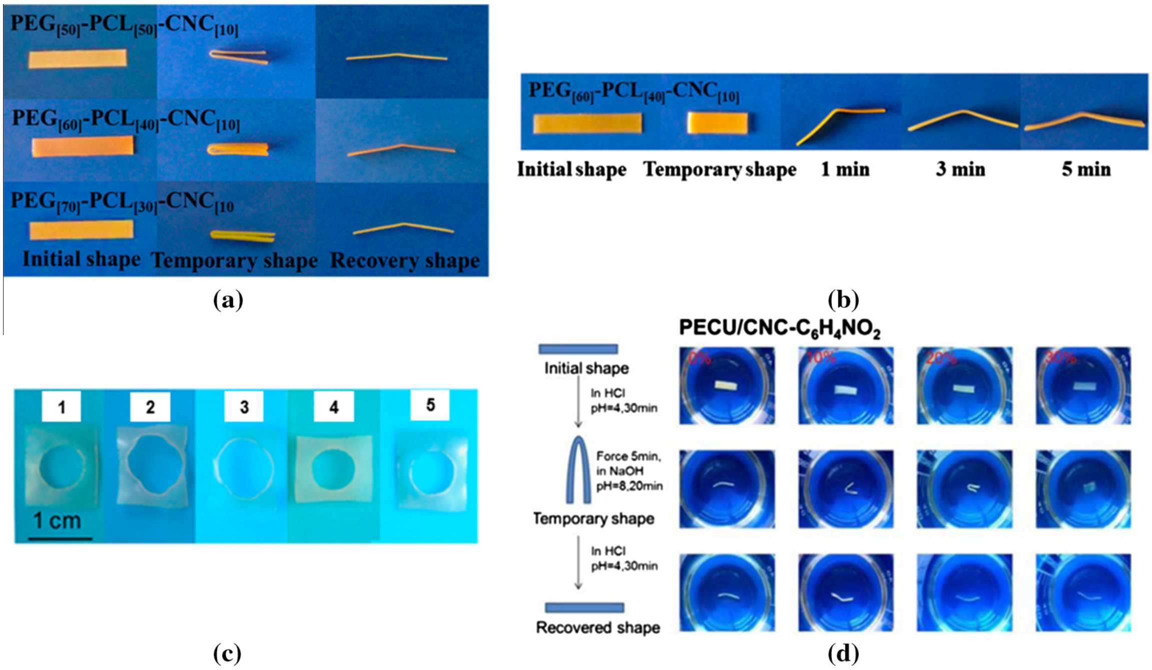

Fig. 14. SMCs materials containing CNCs: (a) Thermo-responsive shape recovery behavior of the PEG-PCL-CNC nanocomposites when heated in oven at 60 °C, (b) water responsive behavior of the nanocomposites in water at 37 °C, (c) water-active shape-memory effects of pretreated PGSU-CNC: original shape (1, wet form after immersion in distilled), fixed deformed shape (2, dried material), deformed shape at the beginning of immersion in water (3), recovered shape after immersion in water (4), and recovered shape after removal from water (5) and (d) digital photos of the shape memory process of PECU/CNC-$C_6H_4NO_2$ film with different CNC-$C_6H_4NO_2$ loading immersed in HCl (pH 4) and NaOH (pH 8) solution at room temperature. Adapted with permission from Liu et al. [182] copyright 2015 American Chemical Society (a) and (b), from Wu et al. [185] copyright 2014 American chemical society (c) and from Li et al. [186] copyright 2015 American chemical society (d).

hydrophilic CNCs as an active agent, were also prepared using biodegradable poly(glycerol sebacate urethane) (PGSU) [185]. In this study the hydrophilic nanocrystals were grafted along the polymer macromolecule: CNCs got competed with the -OH groups from PGS prepolymer (product of glycerol and sebacic acid polycondensation) to react with the isocyanate groups of hexamethylene diisocyanate in order to form urethane linkages. The presence of CNCs (up to 23 vol%) led to an improvement of the PGSU materials tensile strength and the Young's modulus up to 1040% and 4400%, respectively. The phenomena was explained with the formation of strong interfacial interactions based on hydrogen bonds between CNCs and PGSU in the blend. The shape fixity and shape recovery ratios of the PGSU-CNC nanocomposites increased with the CNCs content and became stable (R_r 98% and R_f 99%) after the first three wetting-stretching-drying cycles, owing to the elimination of the sample processing history and CNCs alignment. Digital images of the water-responsive SME are presented in Fig. 14(c). The materials were lipase enzymatically degradable (weight loss of 17% in 28 days), which favors their potential application as implants for minimally invasive medicine.

Functionalized CNCs can be used effectively for the production of pH-responsive SMCs by blending poly(ethylene glycol)-poly(ε-caprolactone)-based polyurethane (PECU) [186]. By modifying the nanofiller surface with pyridine moieties [CNC-$C_6H_4NO_2$] it was possible to create pH-sensitive CNCs percolation network in the polymer matrix, acting as the switch units of the materials. The explored working idea here was that at high pH value, the CNC-$C_6H_4NO_2$ had attractive interactions from the hydrogen bonding between pyridine groups and hydroxyl moieties. At low pH value, these interactions were reduced or disappeared due to the protonation of pyridine groups (Lewis base). Therefore, the hydrogen bonding interactions can be easily disassociated by altering the pH-environment values monitoring the pH-responsiveness of the nanofillers and the materials shape-memory responsiveness (Fig. 14(d)). The CNCs containing SMCs were characterized by improved mechanical properties and can be potentially developed into a new smart polymer material (biomaterials, smart actuators, and sensors).

Segmented thermoplastic PUs are an interesting class of polymer due to the great possibility to modify the chemical structure of their segments: soft segments as a switching segment in SMP and hard segment as a permanent shape responsible. This design offers the advantage to synthesize SMP systems with different molecular architectures and properties. Inspirited by this idea, CNCs were incorporated as a hard segment in PU bionanocomposites in order to improve their mechanical properties [187]. As a result of the thermodynamic incompatibility between both segments, microphase separation of PU/CNCs bionanocomposites was obtained. This was responsible for the presence of two main transitions: soft and hard phase melting temperatures. It was found that the addition of the CNCs led to an increase in the hard phase-crystallinity and improvement of the storage modulus and the shape recovery performances. The mechanical properties of poly(mannitol sebacate) (PMS) network were also enhanced by the incorporation of 5 wt% CNCs (six-fold increase in Young's modulus and five-fold improvement in toughness) [188]. This effect was related to the presence of the hydroxyl groups in the CNCs surface that efficiently interacted with the polymer matrix. The SME of the PMS containing nanocomposites was in the range of physiological temperatures, which makes them also potentially useful for biomedical applications (soft tissue engineering scaffolds).

3.5. SMCs containing other nanofillers

In the literature, it was found that the SMPs properties can be reinforced by the incorporation of other less studied (nano)-fillers such as: microfibers, fabrics and Kevlar mats, carbon or glass fibers. Due to their high elastic modulus, strength and characteristic structural morphology (fiber axial directional disposition) they are capable of ensuring higher mechanical load while maintaining the transverse direction [189]. SMCs containing such nanofillers were described with potential application in the production of spacecraft self-deployable and vibration control structures [40,190,191]. Exfoliated nanoclay as additional hard phase can also reinforce the materials mechanical and shape memory properties [192–194]. Alternative SMPs nanofillers are the SiC and SiO_2 particles. This structures were previously used as cross-linking agent after their surface modification with PCL [195] or coupling with SMPU chains [196].

4. Future directions and challenges

Based on the previously described progress in the field of SMCs production, several future directions and related challenges may be considered:

(i) During the years it has been demonstrated that the incorporation of different nanostructured fillers (nanotubes, nanofibers, NPs, NRs, NWs, NWrs, nanocrystals, etc.) in the SMP-matrix allows the enhancement of the materials mechanical properties. Despite the confirmed research progress, it should be noted that in some cases of direct practical application, the new polymer devices remain with relatively poor mechanical properties. To overcome this difficulty additional efforts are needed to optimize the nanofillers dispersion and the materials characteristics on structural fatigue, relaxation, creep and duration.

(ii) Due to the important impact on human health, the fabrication of biocompatible and biodegradable SMPs medical devices is of great interest. Such materials include scaffolds for tissue engineering, implants for minimally invasive surgery procedures, self-tightening sutures, self-retractable and removable stents, drug delivery systems, synthesis of protein-polymer or DNA-polymer conjugates for therapeutic. Here the main challenges concern the materials rate of degradation (enzymatic or hydrolytic) their degree of toxicity, mechanical solicitation, etc.

(iii) Smart materials and structures obtained by three-dimensional manufacturing (3D printing) are another attractive domain to be developed for the near future. The change in the structural reconfiguration over time upon external stimuli gave the emergence of novel '4D printing' procedure. This allow the production of SMCs as actuators for soft robotics, self-evolving structures, anti-counterfeiting system, active origami and controlled sequential folding as well as 4D bio-printing materials (living biological 3D structures such as tissues, organs and cells or bio-origami hydrogel scaffolds). Some technological and design limitations remain still unsolved such as: limited choice of polymer to be used, multi-material components fabrication, presence of microstructural defects and materials real time adapting.

(iv) Inspired by nature, the design of self-cleaning, self-healing and self-adapting SMPs materials is gaining increased interest over the last few years. These materials are 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. The production of nanocomposites with multi-step responsive self-based capabilities and improved durability will further improve the performance in the field. However none of those polymer systems are commercially available at present and development of new polymers and polymer blends is needed.

(v) Strong interest of both academic and commercial researchers present the energy harvesting SMCs such as visible light-responsive SMPs (solar energy) and chemical-responsive SMPs (chemical reaction energy). The molecular, gas or sound sensible materials can be defined as forthcoming nanocomposites materials. Wireless and remote-controllable SMCs are another class of devices to be produced (magnetic and light actuated composites and pizeo-electrics containing materials).

(vi) In the industry, currently these materials find 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. Despite their multi-functionality and large range of properties the direct transfer from the laboratory to industrial scale remain difficult. In this direction the main problems are the final SME complexity affected by many factors such as the programming step and the triggering process parameters. In addition a quick and versatile manufacturing process is needed, while focusing on use of low-cost additives and ensured profit gain, etc.

5. Conclusion

In the present review a short overview on the SMPs conception, fabrication, modeling during the last twenty years was described. A special attention was paid on the production of new generation SMP materials with multi-responsiveness by the incorporation of nanosized fillers such as carbon-based, noble metal-based nanostructures, metal oxide, and cellulose nanocrystals. The produced SMCs were mainly studied for their enhanced mechanical, thermal and shape recovery properties. Moreover, the new materials were described as sensitive to a great range of stimuli such as electrical current, light, magnetic field, water, solvents, etc. As a conclusion, SMCs have greatly evolved during the past couple of years, particularly in terms of new polymer devices with desired properties and functions. Given the SMCs advantages and multi-functional behavior, we expect them to become one of the leading research subject on smart materials production in near future.

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Florence Pilate obtained her Master in chemistry from the University of Mons in 2013. She is currently pursuing her doctoral degree as F.R.S-FNRS Research Fellow at the Laboratory of Polymeric and Composite Materials under the supervision of Dr. J-.M. Raquez and Prof. P. Dubois. Her main research activities focus on the design of new shape-memory polymer materials with multi-shape and multi-stimuli properties.

Antoniya Toncheva received a master's degree in Structural biochemistry (Bordeaux, France) in 2008 followed by a PhD degree in Macromolecular chemistry within the Laboratory of Bioactive Polymers (LBAP, BAS) in 2012 under the supervision of Prof. I. Rashkov. In 2013 she held an assistant professor position with the LBAP. Starting from January 2015 she moved to the University of Mons (Belgium) under the supervision prof. Ph. Dubois for post-doctoral research (BEWARE Academia Marie Curie Actions). Her current scientific focus is on production of micro- and nanostructured materials from biocompatible and biodegradable polymers by electrospinning and reactive extrusion, their characterization, shape-memory properties and potential biomedical application.

Philippe Dubois is full professor at University of Mons (UMONS, Belgium) and director of the Center of Innovation and Research in Materials & Polymers. His expertise covers organic chemistry, macromolecular chemistry, catalysis in polymer materials, melt (reactive) processing/engineering of nanocomposite and nanohybrid materials, incl. biodegradable and biosourced polymers. He has published +630 peer-reviewed scientific articles and is inventor of 66 patents. He is scientific director of Materia Nova research center located in Mons. In 2011, he created a university spin-off Cie named NANO4 S.A., active in production, functionalization and characterization of nanoparticles and their applications as nanofillers in polymer nanocomposites and sol-gel coatings. He is elected titular member of the Royal Academy of Sciences, Belgium.

Jean-Marie Raquez, Ph.D. in Polymer Science, is currently a FNRS-FRS research associate at University of Mons (Belgium) within the Center of Innovation and Research in Materials and Polymers (CIRMAP, ca. 160 persons) and Scientific Coordinator at Materia Nova (Mons, Belgium). His main areas are the chemical modification and synthesis of polymer-based (nano)-composites derived from renewable resource using reactive extrusion processing. In the realm, he has more than ca. 85 peer-reviewed publications in international journals, 30 personal communications at conferences and is co-inventor of seven patents. He has co-edited one book and six chapters of a book.