Smart polymer nanocomposites: A review

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Abstract. The development of smart polymer nanocomposites (SPN) has been an area of high scientific and industrial interest in recent years, due to fantastic improvements achieved in these materials. SPN found potential applications in shape memory, self-healing, self-sensing, self-heating, self-cleaning, and energy harvesting. This mini-review highlights the current research and development on SPN, specifically on shape memory polymer (SMP) and self-healing polymer (SHP) nanocomposites. The processing techniques for SPN nanocomposites, for example, polymerization, melt-compounding, solution mixing, electrospinning, and thermoset-curing are discussed. Some of the potential strategies to modify the properties of SMP and SHP nanocomposites are highlighted. The future perspective and recommended works for the SPN nanocomposites are shared in this mini-review.

Keywords: smart polymers, nanocomposites, shape memory polymers, self-healing polymers

1. Introduction

The smartness of material development always comes from the inspiration and intelligence of nature. Smart materials can be defined as materials that incorporate the functions of sensing, actuation, and control [1, 2]. Smart materials are attracting increasing interest especially in the era of the fourth industrial revolution (Industry 4.0) and circular economy. Smart polymer nanocomposites (SPN) which can be derived from shape memory polymer [3–6], stimuli-active polymers [7], smart electrorheological (ER) and magnetorheological (MR) polymer [8–11], self-healing polymer [12, 13], self-cleaning polymer [14–17], self-heating polymer [18], self-sensing polymer [19], energy-harvesting and energy storage polymer [20–27] are the latest hot research topics. The addition of nanofiller can increase the performance of the SPN (e.g., shape fixity, shape recovery, self-healing ability) due to their high specific surface area, nucleating

effects, reinforcing effects, and inherent functionalities (e.g., thermal conductivity, electrical conductivity) [3]. SPNs are widely used in various applications, for example, sensor and actuator [28–33], stretchable electronic [34], wearable electronics, and smart textiles [35, 36], drug carrier and delivery [37, 38], aircraft and aerospace applications [39, 40].

Ten years ago, Ratna and Karger-Kocsis [41] has documented a review on shape memory polymers and composites. When revisiting the ‘future outlook’ from Ratna and Karger-Kocsis [41], they ‘forecasted’ that the blending and interpenetrating network-based polymers in SMP could have lead to the development of newer and novel SMPs. They also ‘predicted’ that SMPs are going to be the future materials for deployable structures for aircraft and spacecraft applications. And, nowadays there are numerous research publications dealing with SMP via blending and interpenetrating network strategies.

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This mini-review on smart polymer nanocomposites is mainly focused on the shape memory polymer (SMP) and self-healing polymer (SHP), which is part of the ‘heritage’ from Professor Karger-Kocsis. This article provides a basic fundamental and idea on how to fabricate SPN with different types of processing techniques. This could benefit for researchers (especially ‘beginners’) who are looking for feasible method to synthesis and prepare SPN, using as simple as solvent casting and melt blending, to some sophisticated methods (*e.g.*, electrospinning, 3D and 4D printing).

2. Smart polymer nanocomposites

2.1. Shape memory polymer

Shape memory polymer (SMP) possesses the capability to fix temporary shape and recover its original shape upon subjected to external stimuli. The stimuli for shape memory alloy (SMA) is always limited to heat (*e.g.*, Joule heating) and magnetic field, whereas there are more ‘triggering choice’ for SMP, *e.g.*, light, water, solvent, pH, temperature, electricity [42–46].

Furthermore, compared with SMA, most of the SMP has more advantages, for example, low density, high elastic deformation, good biocompatibility and biodegradability, as well as fantastic tailor-ability.

In general, SMP consists of permanent net-points (a stable polymer network) and molecular switches of reversible nature. The former memorizes the original shape while the latter are used for setting the temporary shape [47, 48]. The permanent net-points of SMP can be formed by molecule entanglement, crystalline phase, chemical cross-linking, or interpenetrated network. Normally, thermo-sensitive SMP containing physical (or chemical) network-points, which determine their original shape, while each temporary shape is fixed by switching domains associated to a thermal transition temperature (T_{trans}), which can be crystallization/melting transition, vitrification/glass transition, liquid crystal anisotropic/isotropic transition, reversible molecule cross-linking, and supramolecular association/disassociation [49]. The essential performance parameters for an SMP include T_{trans} , shape fixity ratio (R_f) and shape recovery ratio

Figure 1. Molecular mechanisms of the thermally-induced one way shape memory (1W-SM) effect in amorphous linear (thermoplastic) and crosslinked (thermoset) polymers. Note: temporary shape is created by tensile deformation (reproduced from Karger-Kocsis and Kéki [51]).

(R_f). The viscoelastic and relaxation behaviors of SMP are attributed to the cooperative relaxation of each component. The working mechanism in the thermo-responsive SMP is governed by both of the internal recovery stress and stored mechanical energy [50]. Figure 1 shows the molecular mechanisms of the thermally-induced one way shape memory effect in amorphous linear thermoplastic and crosslinked thermoset polymers [51]. The polymers that are used for designing shape-memories are divided into thermoplastic and thermoset. In general, thermoset SMPs can store more energy and endure more cycles (shape-changing) than thermoplastic ones due to the cross-linked bonds. Nonetheless, thermoplastic SMP can be manufactured by a facile processing method [52]. Figure 2 shows general shape memory behavior of thermally triggered SMP [53]. At heating of programmed samples, the viscoelastic forces and stored entropic will be used for recovery of temporary shape back to original shape, while the T_g or T_m is used for switching mechanism.

Conventionally, SMP can be triggered by single- and/or dual-stimuli. Nowadays, SMP can be triggered by multiple stimuli. Consequently, multi-responsive SMP is more fascinating and thus, it gives more

opportunity to be used in diversified applications [54]. The introduction of nanofiller to SMP can unlock their potential for the integration of multiple stimulus methods, such as electro-activated, magnetic field actuated, light-responsive, near-infrared activated, water-induced, and thermal-responsive [55, 56]. Nanofillers can improve the mechanical performance and shape recovery stress of SMP through physical blending, *in-situ* polymerization and chemical cross-linking [49]. For example, the addition of carbon nanotube (CNT) and graphene nanoplatelet is capable of converting the electrical current into heat through Joule effect and thus actuating the SMP [3]. SMP nanocomposites can be used in electrochemical devices, biomimetic devices, actuators and sensors, active sound-absorbing materials, smart textiles, smart windows, deployable space structures, morphing aircraft, artificial muscle, civil and architecture applications [57, 58].

SMP based on biopolymer is worth to mention because this kind of successful SMP can offer good biodegradability and compostability, which is in line with sustainable development [59]. Karger-Kocsis and Kéki [51] had documented a review of biodegradable polyester-based shape memory polymers. SMP

Figure 2. General shape memory behavior of thermally triggered polymer material (reproduced from Kolesov *et al.* [53]).

Figure 3. Schematic diagram of thermally responsive SMP in heat controls of window blinds (reproduced from Li *et al.* [60]).

based on biodegradable polyesters that are designed for medical devices application (*e.g.*, sutures, stents, catheters) should be present only temporarily in human body. The future development of biodegradable polyester–SMP should focus on switching temperature for human body, improvement of shape memory effect (*e.g.*, shape recovery), degradability and recyclability.

For readers to understand the SMP usage in daily life, here we show an example of SMP used in window blinds, which is documented in the review by Li *et al.* [60]. One of the feasible approaches to enhance building energy efficiency is to develop dynamic building envelope systems that can tune their thermal and optical properties based on seasonal or daily climatic changes. In this context, the external stimuli can be the sun positions, solar radiation levels, temperatures, and humidity. Figure 3 shows a schematic diagram of thermally responsive SMP in heat controls of window blinds. The angles of the blind slats can be ‘self-adjusted’ (actuated) according to the different external air temperatures during winter and summer time.

2.2. Self-healing polymer

Self-healing polymer (SHP) is one type of smart materials that can demonstrate healing-ability, *in-situ* damage repairing, and properties restoring. This prolongs the service life, enhance the product reliability, reduce the frequency of scheduled inspection, and lower the maintenance cost of the composite structures [61, 62].

There are two ways of healing strategies: (i) intrinsic self-healing and (ii) extrinsic self-healing. The former is able to heal the damage (*e.g.* cracks) by the polymer itself, where the inherently thermally reversible

bonds of the material create a healing effect under external heating; while the latter is pre-embedded with healing agent (*e.g.*, microcapsules, microvascular networks, hollow fibers) [63, 64].

Self-healing technology can be applied for thermoplastic and thermoset systems. Vijayan and Al-Maadeed [65] had documented a review on the self-healing epoxy composites and coating. The nature of the ‘container’ (which containing healing agent) such as the material, shell wall thickness, storage stability, and its response to the external stimulations (*e.g.*, mechanical impact) are of great importance in determining the self-healing efficiency.

To demonstrate the extrinsic self-healing technology and the importance of nanofiller for SHP nanocomposites, here we give an example of SHP nanocomposites for outer space application. One of the major challenges for space missions is that most of the materials degrade over time under extreme environments. Aïssa *et al.* [66] had investigated self-healing materials on composite structures used in space environment. The self-healing materials were microcapsules containing 5-ethylidene-2-norbornene and dicyclopentadiene monomers with ruthenium Grubbs’ catalyst. The self-healing materials were then mixed with an epoxy resin (epoxy prepolymer Epon 828 and curing agent Epicure 3046) and single-walled carbon nanotubes (SWCNT; loading: 2 wt%) by using vacuum centrifuging technique. The obtained SHP nanocomposites were infused into the layers of woven carbon fibers reinforced polymer (CFRP). The CFRP specimens were then subjected to hypervelocity impact conditions, which is prevailing in the space environment using a home-made implosion-driven hypervelocity launcher. Figure 4 shows a typical example of color code diagram obtained for CFRP with and without SHP nanocomposites. The thickness distribution of the CFRP with SHP nanocomposites is much more homogenized compared to that of CFRP (with pure Epon 828), which indicates a good healing effect (*i.e.*, less delamination propagation after the healing process). The healing efficiency of the CFRP (4 layers woven fiber) with SHP nanocomposites is about 83%.

Intrinsic self-healing materials can undergo self-healing processes multiple times through dynamic non-covalent interactions (*e.g.*, hydrogen bonds, π – π stacking) and dynamic covalent bonds (*e.g.*, urea bonds, Diels–Alder bonds). Self-healing materials based on dynamic covalent bonding have advantages

Figure 4. (a) Optical photo of the CFRP structure after impact tests, (b) representative cross-sectional view optical photos of the CFRP sample. Color code diagram simulation of the impacted sample in cases (c) with and (d) without self healing materials (reproduced from Aïssa *et al.* [66]).

such as high strength, increased thermal stability, and solvent resistance compared to self-healing materials based on non-covalent interactions. Zhao *et al.* [67] had prepared self-healing polysiloxane nanocomposite using furan-functionalized graphene as reinforcement based on Diels–Alder (DA) chemistry. The healable polysiloxane nanocomposite recovered more than 90% tensile strength and 98% elongation at break. The excellent self-healing efficiency is achieved by the reversible DA bonds between furan-functionalized graphene and polysiloxane chains. The above mentioned intrinsic self-healing technology is potential to fabricate SHP nanocomposites with high healing performance and improved mechanical properties.

The self-healing efficiency is one of the performance indicators for the SHP nanocomposites. The effectiveness and efficiency of self-healing for SHP nanocomposites are controlled by a number of factors, *e.g.*, the polymer matrix, the selection of nanofiller, the choices of self-healing mechanism (intrinsic or extrinsic), and the environment [68]. The concept of self-healing for other materials, *e.g.* cement and concrete in the

construction industry (*e.g.*, the using of extruded cementitious hollow tubes as containing/releasing devices for healing agents) and nature creatures (*i.e.*, self-healing of starfish) can be used as an additional ‘reference’ for the development of SHP nanocomposites.

3. Processing-microstructure-property

It is quite reasonable if one mentions that most common methods used to synthesize and produce polymer nanocomposites can be used to fabricate SPNs. It is important to understand the basics of SMP and SHP nanocomposites. This mini-review gives an insight into the preparation and properties of SMP and SHP nanocomposites. Standard processing techniques including polymerization, melt blending, and solution mixing are discussed. Some of the specific preparation methods, *e.g.*, hydrogel, electrospinning, and thermosetting are also introduced.

3.1. Polymerization

In the open literature, there is a number of researchers using *in-situ* polymerization to prepare polymer

nanocomposites. In this mini-review, some of the current research works on synthesis of SPN are documented. You *et al.* [69] prepared temperature-responsive poly(*N*-isopropylacrylamide) (PNIPAM)-multi-walled carbon nanotube (MWCNT) conjugates via stimuli-responsive linkages by combination reversible addition-fragmentation chain transfer (RAFT) polymerization and thiol-coupling reaction. The PNIPAM-MWCNT nanocomposites are sensitive to both temperature and bio-stimuli (*e.g.*, glutathione concentration). Biological molecules (*e.g.*,

protein, deoxyribonucleic acid (DNA), peptide) are easily attached to carbon nanotubes (CNT) via a disulfide bond, and it can be released from CNT in the presence of external stimuli. This is important to widen the potential application of CNT vector in nano-biotechnology, nano-medicine, and drug delivery.

Narendra Kumar *et al.* [70] explored the thermally and magnetically initiated shape-memory properties of triple-shape nanocomposites using different shape-memory creation procedures (SMCP). The SMP

a)

b)

Figure 5. (a) Schematic representations of the different shape-memory creation procedures applied for bending of the nanocomposites. Two-step programming methods: SMCP-2s-I, SMCP-2s-II as well as single-step programming procedure SMCP-1s. (b) Molecular mechanism for graft polymer network composites during shape-memory creation procedure where the color indicating the different phases of the polymer segments. Orange: amorphous PCL chain segments, Light blue: amorphous PEG chain segments, Red: crystalline PCL chain segments, Dark blue: crystalline PEG chain segments, Grey: amorphous poly(methacrylate) chain segments (reproduced from Narendra Kumar *et al.* [70]).

nanocomposites consisting of crystallizable poly(ethylene glycol) (PEG) side chains, poly(ϵ -caprolactone) (PCL), and silica-coated magnetite nanoparticles. The nanocomposites with high PEG content achieved excellent triple-shape memory effect when two-step programming procedures are used. Figure 5 shows the schematic diagrams of the various SMCP applied for bending of the nanocomposites and their molecular mechanisms [70].

Cai *et al.* [71] prepared PCL/polyurethane (PU)/Fe₃O₄ SMP nanocomposites by the *in-situ* polymerization method. The temperature at 45 °C was selected as shape recovery temperature based on the consideration of the potential clinical application of the SMP nanocomposites. It is found that PCL/PU/Fe₃O₄ SMP nanocomposites exhibited high shape recovery rate at 45 °C. Furthermore, in the alternating magnetic field ($f = 45$ kHz, $H = 35.7$ kA·m⁻¹), the shape memory properties of the PCL/PU/Fe₃O₄ SMP nanocomposites were improved by the increasing loading of Fe₃O₄, with the best recovery rate achieved 97%. This suggested the potential application of PCL/PU/Fe₃O₄ SMP nanocomposites for magnetic sensitive biomedical devices.

Kalita and Karak [72] prepared Mesua ferrea L. seed oil-based hyperbranched polyurethane (HBPU)/Fe₃O₄ nanocomposites by *in-situ* polymerization technique. The HBPU nanocomposites possess full shape fixity and nearly full shape recovery under the application of microwave stimulus (microwave output power = 350 W). This is attributed to the frozen micro-Brownian movements of molecular chains during the vitrification. Note that the shape recovery speed increases with the increasing loading of Fe₃O₄ nanoparticles. Gao *et al.* [73] prepared biodegradable magnetic-sensitive shape memory PCL/ γ -(methacryloyloxy)propyl trimethoxysilane functionalized Fe₃O₄ magnetic nanoparticles (MNP) via *in-situ* polymerization method. In hot water bath ($T = 60$ °C), the shape recovery rate and shape fixity rate of the PCL/silane functionalized Fe₃O₄ SMP nanocomposites recorded 98 and 100%, respectively. In an alternating magnetic field ($f = 60, 90$ kHz, $H = 38.7, 59.8$ kA·m⁻¹), the SMP nanocomposites achieved shape recovery rate in the range of 85 to 95.3%. This is due to the fact that the silane functionalized Fe₃O₄ MNP can act as net-points in the network, and consequently spread out the heat uniformly in the SMP nanocomposites.

Kurd *et al.* [74] synthesized poly(*N*-isopropyl acrylamide-methacrylic acid-hydroxy ethyl methacrylate)

(P(NIPAm-MAA-HEM)) by emulsion polymerization. Fe₃O₄ MNP and cisplatin (an anticancer chemotherapy drug) were loaded onto the nanogel by a swelling method. The P(NIPAm-MAA-HEM) nanocomposites show high drug release at low pH and high temperature, which are the conditions relevant to the cancer medium during hyperthermia.

Ahmadkhani *et al.* [75] synthesized dual responsive SNP from PEG, poly(methacrylic acid) (PMA), PNIPAm, and Fe₃O₄ nanoparticles using RAFT polymerization. The poly[(PMA-PNIPAm)*m*-*b*-PEG-*b*-(PNIPAm-PMA)*m*] triblock terpolymer micelles were capable of encapsulating doxorubicin (DOX, a common chemotherapeutic drugs). The release rate experiments of the DOX-loaded magnetic nanocomposite in two different phosphate-buffered saline (PBS) solution (pH = 5.8 and 7.4) were performed at 37 and 42 °C. Under acidic conditions (pH < pK_a), the occurrence of carboxylate anions protonation in the PMA chain leads to the breaking of electrostatic interaction between PMA and DOX, and thus promoted the drug release from the nanocomposites.

Lakatos *et al.* [76] synthesized segmented linear PU containing Diels-Alder (DA) adduct in toluene solution from PCL (molecular weight, $M_n = 10, 25$ and 50 kg/mol), methylene diphenyl diisocyanate (MDI), 2,4-toluene diisocyanate (TDI), 1,6-hexamethylene diisocyanate (HDI), furfurylamine (FA) and bis-maleimide (BMI). The PCL(10)-MDI-FA-BMI (monomer ratio = 1:3:2:2) and PCL(25)-MDI-FA-BMI (monomer ratio = 1:3:2:2) exhibited shape fixity of 99 and 100%, respectively after deformation at 80 °C for 80% strain. Dynamic mechanical analysis (DMA) results demonstrated a plateau-like region above T_m of PCL, and this suggested the existing of a physical network where the net-points are provided by the DA couplers-hard segments.

Abbasi *et al.* [77] synthesized biocompatible PU/graphene nanoplatelet (GNP) nanocomposites from poly(ϵ -caprolactone)diol (PCL diol)/castor oil and HDI by using *in-situ* polymerization. The shape fixity of the PU/GNP nanocomposites is governed by the degree of crystallinity and glassy modulus. Higher loading of GNP increased the shape fixity of the nanocomposites remarkably. Besides, the shape recovery of PU/GNP (loading = 1.5 wt%) recorded at 99%, which is much higher than that of pure PU (shape recovery = 91%). This is attributed to the chemical bonding of GNP and hard segment in the PU nanocomposites.

Liu *et al.* [78] prepared poly(methyl methacrylate) (PMMA)/PEG semi-interpenetrating network [PMMA-PEG semi-IPN] by using radical polymerization and crosslinking of methyl methacrylate (MMA) in the presence of 2,2'-azoisobutyronitrile (AIBN) initiator, ethylene glycol dimethacrylate (EGDMA) cross-linker and linear PEG. The PMMA-PEG semi-IPN exhibits two independent shape memory effects based on the T_m of the PEG crystals and the T_g of the semi-IPN. It was found that the PMMA-PEG semi-IPN demonstrated an excellent recovery ratio of 99%. In another study, Liu *et al.* [79] prepared poly((methyl methacrylate)-*co*-(*N*-vinyl-2-pyrrolidone))/PEG semi-IPN [P(MMA-*co*-NVP)/PEG semi-IPN] by radical copolymerization of MMA with NVP in the presence of AIBN initiator, EGDMA crosslinker and linear PEG. The crosslinked P(MMA-*co*-NVP) networks were acted as the fixed phase, whereas the amorphous PEG-PVP complex phases function as the reversible phase. The P(MMA-*co*-NVP)/PEG semi-IPN prepared using the concept of hydrogen bonding interaction, could give SMP nanocomposites with a recovery ratio of 99%.

Ghosh and Karak [80] fabricated IPN-based SPN from PU, polystyrene (PS), polystyrene grafted MWCNT (PS-*g*-MWCNT). The pristine PU/PS IPN only can heal at high microwave power input (450 W). Interesting to note that the PU/PS IPN containing PS-*g*-MWCNT/MWCNT exhibited excellent self-healing ability under the exposure of microwave (within 46–22 s at 300 W power input) and sunlight (within 318–257 s, light intensity: $0.9\text{--}1.1 \cdot 10^5$ lux). The PS-*g*-MWCNT can serve as a nano-heater in the IPN attributed to its high thermal conduction. The Brownian motions of the soft segment increase with the increasing loading of the PS-*g*-MWCNT. The higher the MWCNT loading, the higher the healing efficiency is.

3.2. Melt compounding

Melt processing is environmentally friendly (often solvent-free) and viable for commercial and industrial expansion. The manufacturing of polymer nanocomposites using melt compounding is a common approach. It can be achieved by readily available mixing and molding equipment, *e.g.*, extrusion and injection molding. Yan *et al.* [81] melt mixed polylactide-based copolyester (PLAE) with silane coupling treated nano-SiO₂ using an intermeshing twin-screw extruder followed by injection molding. The

polytetramethylene ether (PTMEG) chains and the amorphous phase of PLA are function as the soft parts, while the crystallization phase of PLA segments and nano-SiO₂ are act as fixed parts of the shape memory PLAE when the temperature is above 35 °C. PLAE and its nanocomposites with low SiO₂ loading content (1 and 3 wt%) possess good shape fixity (more than 95%) and recovery ratio (more than 87%) with a trigger temperature around body temperature. The shape recovery is triggered by glass transition of polylactic acid (PLA) chain segments. The PLAE nanocomposites could have potential applications in biomedical areas such as smart punctual plugs because of their low trigger temperature.

Gu *et al.* [82] prepared low T_g ester-based PU ($T_g = -34$ °C)/carbon nanotube (both pristine CNT and oxidized CNT) using melt mixing (mixing temperature: 185 °C; rotor speed: 30 rpm; mixing time: 20 min). This kind of ester-based PU is suitable to be used to develop SMP nanocomposites with low trigger temperature, which have potential applications for controlling tags or proof marks in the area of frozen food. The ester groups of polyol soft segments function as reversible phases, while the elastomeric networks of the PU which consisting of hydrogen-bonded urethane linkages act as fixed phases. Note that CNT (both pristine and oxidized) also can serve as an additional fixed phase due to the interaction between the CNT and the PU matrix. The shape fixity and shape recovery of the PU nanocomposites recorded above 98% for the second tensile cycle. It is worth to mention that the PU/oxidized CNT nanocomposites showed faster recovery compared to that of PU/untreated CNT counterparts. This indicates that the incorporation of oxidized CNT could promote and accelerate the recovery process due to its higher energy stored in the temporary shape.

Navarro-Baena *et al.* [83] prepared poly(ester-urethane)/poly(L-lactic acid) grafted cellulose nanocrystals (CNC-*g*-PLLA). The strain recovery and strain fixity ratio of the bionanocomposites are about 90%. The improvement in the shape memory behavior is mainly attributed to the improvement in the interactions between the CNC-*g*-PLLA and the poly(ester-urethane). Sessini *et al.* [84] prepared SiO₂ nanoparticles reinforced poly(ethylene-*co*-methacrylic acid) copolymer (PEMAA) and ionomers nanocomposites (its counterpart neutralized with sodium salt, PEMA-*Na*) nanocomposites using micro-extruder equipped with twin conical co-rotating screws

(temperature = 150 °C; screw rotation speed = 130 rpm; residence time = 5 min). The PE primary crystals and the amorphous phase are function as permanent network (memorizing the original shape) while the PE secondary crystals act as switching network (fixing the temporary shape). PEMA-Na ionomer nanocomposites (silica loading = 1 wt%) showed excellent shape memory properties reaching maximum values of about 96 and 98% for strain recovery rate and strain fixity rate, respectively.

Eshkaftaki and Ghasemin [85] prepared PMMA/PLA/GNP nanocomposites by using an internal mixer (mixing temperature: 180 °C; rotor speed: 60 rpm; mixing time: 10 minutes). At 100 °C, the shape recovery of the PLA/PMMA was increased from 93.3 to 96.7% by the addition of 1 phr of GNP. However, there are not many changes in the shape recovery of the nanocomposites at 65 °C. A higher degree of crystallization of PLA and higher storage modulus were obtained attributed to the nucleation and reinforcement effects of GNP, and these lead to

the enhancement of the shape fixity of the PMMA/PLA/GNP nanocomposites.

3.3. Solution mixing

Solution mixing is a straightforward method to prepare polymer nanocomposites, especially for a soluble polymer. The dispersion of nanofiller in the polymer prepared using solution mixing can often be enhanced by using ultra-sonification. In some of the research works, solution mixing methods are used to fast-screening for the development of polymer nanocomposites. Nevertheless, the solvent evaporation and environmental issue should be concerned. Solution casting technology has been used for the production of engineering plastics, and optical films. The advantages of this technology include uniform thickness distribution and high optical purity. Lashgari *et al.* [86] prepared PLLA/GNP using solution casting technique. The infrared actuated shape memory ratio of PLLA was increased from 86 to 95% by the addition of GNP. This is because the GNP can absorb

Figure 6. Temperature distribution snapshots of pure PLLA and its nanocomposites during infrared actuation recovery (reproduced from Lashgari *et al.* [86]).

infrared wave's energy and activate the shape memory of the PLLA nanocomposites. Figure 6 shows the thermo-camera images of a free recovery process in the pure PLLA, PLLA/GNp1 (PLLA filled with 1 wt% GNp) and PLLA/GNp6 (PLLA filled with 6 wt% GNp) nanocomposites actuated by infrared radiation. At 20 seconds, pure PLLA does not start recovering, but PLLA-GNp6 recovered about 90%. This is due to more infrared energy is absorbed and transformed into thermal energy, in the presence of GNp.

Luo *et al.* [87] prepared shape memory polyurethane (SMPU) by mixing the cellulose nanowhiskers (CNW) suspension with SMPU solution in *N,N*-dimethylformamide (DMF). The PCL-diol segments function as thermally sensitive switch (due to the melting/crystallization transition), while the CNW percolation networks act as a water-sensitive switch (due to the reversible responsiveness to water). Consequently, the SMPU/CNW nanocomposites exhibited twin-switchable shape memory effect when applied to an aqueous-thermal-program.

Ahmed *et al.* [88] prepared electrically conductive MWCNT filled PU/modified PS blends using solvent casting method. The PU/modified PS/MWCNT nanocomposites demonstrated outstanding thermal- and electric field-triggered shape memory behavior to the extent of 95 and 96%, respectively. The shape recovery enhancement of the PU nanocomposites was provided by CNT and the network strengthening via hydrogen bonding and urethane linkages. Zhong *et al.* [89] prepared gold (Au) nanoparticle filled PNIPAm-block-polypyrrole copolymer (PNIPAm-*b*-PPy) nanocomposites using amphiphilic PNIPAm-*block*-poly(pyrrolyl-methylstyrene) (PNIPAm-*b*-PPMS) diblock copolymers as ligands. The PNIPAm-*b*-PPy/Au nanocomposites exhibit photo-thermal effect based on strong absorption in the NIR region (due to PPy photo-thermal effects) and reversible, soluble-precipitate transition upon NIR irradiation 'on-off' (due to PNIPAm thermo-sensitive effects).

Qian *et al.* [90] fabricated vapor-grown carbon nanofibers (VGCNF) filled poly(ethylene-co-vinyl acetate) (EVA) nanocomposites through solution mixing to obtain electrical-active two-ways SMP nanocomposites. The expanding and refolding of EVA/VGCNF (mass fraction = 15%) nanocomposites (in strip form) can be repeated by controlling the power

switch, and thus make it suitable to be used as smart actuators.

Molavi *et al.* [91] prepared thermally actuated triple-SMP nanocomposites based on PLA/PCL/functionalized GNp by using solution mixing method. The melting points of crystalline phases were selected as transition temperatures (T_{trans}), and triple-shape memory was induced at $T_{m, PLA}$, and $T_{m, PCL}$. The PLA offers the hard phase for shape fixity while PCL provides the reversible phase for shape recovery. The PLA/PCL nanocomposites showed fixity ratio and recovery ratio, about 80, and 90%, respectively. A higher recovery ratio was obtained by the addition of the thermal conductive GNp (loading = 1.5 wt%). Abbasi-Shirsavar *et al.* [92] fabricated PU/PCL/ZnO nanoparticle nanocomposites by using a solvent casting method. The shape recovery ratio of the PU/PCL nanocomposites was increased by the addition of 20 wt% ZnO. This is because some nanoparticles restrict the hard segment-soft segment interactions and thus gives more mobility to PCL, while the other ZnO nanoparticles act as a nucleating agent for PCL. Gu *et al.* [93] developed a dual-induced self-expandable stent based on biodegradable shape memory PU/Fe₃O₄ nanocomposites by solution casting method. The stent could maintain its temporary shape at body temperature for a certain period while it was able to recover to its permanent shape at the temperature slightly above body temperature (around 40 °C) in both a water bath and an alternating magnetic field. The nanocomposites showed excellent shape memory properties (strain fixity ratio ~ 100%; strain recovery ratio > 82%) at a temperature around body temperature and had considerable strength, appropriate elongation to matching the physical properties of soft biological tissues – which is suitable for biomedical application, such as cardiovascular stents.

Polymer nanocomposites membranes are widely used in water treatment, antifouling nano-filtration, gas separation, wound, and skin dressing. SMP-based skin dressing is attractive due to its unique thermo-responsive phase transition effect. It can be used to fabricate skin dressing that stripped 'automatically', without causing secondary damage on the patient skin. Zou *et al.* [94] prepared temperature-sensitive PNIPAm/konjac glucomannan (KGM)/graphene oxide (GO) nanocomposite membrane by using solution blending, with calcium ions as a cross-linker.

Figure 7. Digital photo of PNIPAm (B1 and B4), PNIPAm/KGM (B2 and B5), and PNIPAm/KGM/GO (B3 and B6) composite membranes with the volume conversion at 25 and 37 °C, respectively (reproduced from Zou *et al.* [94]).

Figure 7 shows digital photo of PNIPAm, PNIPAm/KGM, and PNIPAm/KGM/GO nanocomposite membranes with the volume conversion at 25 and 37 °C, respectively. At temperature below the lower critical solution temperature (LCST), the PNIPAm/KGM/GO nanocomposite membrane was swollen, whereas, at temperature above the LCST, the membrane was shrunk. This indicates that the PNIPAm/KGM/GO nanocomposite membrane is sensitive to temperature and it is potential to be used as smart skin dressing materials.

3.4. Other processing techniques

3.4.1. Hydrogels

Stimuli-responsive nanocomposite hydrogels possess an inherent intelligence and self-adaptation ability when subjected to different external stimuli, *e.g.*, temperature, pH, electric current, light, and ionic strength. Nanocomposite hydrogels have attracted much attention due to their rapid swelling-deswelling response, high swelling ratios, and tunable physical properties [95, 96]. Stimuli-responsive hydrogels are

widely used in numerous potential applications, *e.g.*, sensor, actuators, transducers, artificial muscles, tissue engineering scaffolds, microfluidics, and drug delivery vector [97–101].

Haraguchi [102] had synthesized PNIPAm/water swellable hectorite clay by using *in-situ* polymerization. The addition of hectorite clay increases the stretch-ability of the PNIPAm nanocomposite hydrogel. Furthermore, the coil-to-globule transition temperature of PNIPAm nanocomposite hydrogel can be controlled by using different inorganic salt (*i.e.*, NaCl) concentration and cationic surfactant.

The incorporation of superparamagnetic iron oxide (Fe_3O_4) nanoparticles in stimuli-responsive hydrogel can widen their biomedical application, *e.g.*, protein immobilization, separation, and purification, magnetic resonance imaging, and biosensor. Yassine *et al.* [103] developed a nanocomposite gel consisting of PNIPAm and magnetic Fe_3O_4 nanobeads (NB) for controlled release of drugs upon exposure to an alternating magnetic field. The drug release study was carried out by remotely triggering the

Figure 8. Principle of magnetically controlled drug release using PNIPAm microparticles with embedded iron oxide nanobeads (NB) to form monodispersed magneto-thermo-responsive nanocomposites (MTN). The MTN are fabricated in a microfluidic system and filled with a drug by means of diffusion. The heat generated by the NB upon the application of an alternating magnetic field causes the gel-structure to shrink and the release of drug (reproduced from Yassine *et al.* [103]).

magneto-thermo-responsive nanocomposites (MTN) with an alternating magnetic field of 72 mT in amplitude and 600 kHz in frequency. The principle of the magnetically controlled drug release by using PNIPAm MTN method is shown in Figure 8. It is found that the MTN can de-swell more than 80% of its initial weight within a short time (approximately 6 minutes) under an alternating magnetic field.

Ahmad *et al.* [104] prepared dual temperature- and pH-responsive $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{poly}(\text{styrene-}N\text{-isopropylacrylamide-methyl methacrylate-polyethylene glycol methacrylate})$ [P(S-NIPAm-MAA-PEGMA)] and temperature-responsive $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{poly}(\text{S-NIPAm-methacrylic acid-PEGMA})$ [P(S-NIPAm-MMA-PEGMA)] nanocomposite hydrogel particles by blending $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanocomposite particles with the respective hydrogel particles. Figure 9 shows the absorption behavior of trypsin (a serine protease in digestive system) by $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanocomposite and $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{S-NIPAm-MAA-PEGMA})$ and $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{S-NIPAm-MMA-PEGMA})$ nanocomposite hydrogel at temperature above and below the LCST. It was found that electrostatic attraction among negatively charged $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanocomposite and positively charged P(S-NIPAm-MMA-PEGMA) favors the formation of magnetic nanocomposite hydrogel. Hou *et al.* [105] prepared near-infrared (NIR) laser switched copper sulfide (CuS)/clay/poly(oligo

Figure 9. Bar diagram represents the amount of absorptions of trypsin on (a) $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanocomposite, (b) $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{S-NIPAm-MAA-PEGMA})$ and (c) $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{S-NIPAm-MMA-PEGMA})$ composite hydrogel particles at temperature above (40 °C) and below (20 °C) of the LCST. Absorption: immobilization 200 mg/g of particles, pH 10.0, immobilization time 45 min (reproduced from Ahmad *et al.* [104]).

ethylene glycol methacrylate-*co*-2,2-methoxyethoxy ethyl methacrylate) [poly(OEGMA-*co*-MEO₂MA)] nanocomposite hydrogel by free radical polymerization. The cyclic test results proved that the poly (OEGMA-*co*-MEO₂MA)/CuS/clay nanocomposite hydrogel exhibited stable volume transition properties. A smart liquid microvalve made by the nanocomposite hydrogel has been fabricated, and it could be remotely controlled by NIR switch effectively.

3.4.2. Filament spinning and electrospinning

Smart polymer ultrafine fibers have gained attention attributed to their potential application, such as electronic textiles, dust-free clothing, electromagnetic interference shielding, filtration, and biomedical use [106, 107]. Tonndorf *et al.* [108] prepared a laser light-sensitive yarn based on thermoplastic polyester-urethane/gold nanorods (GNR) by a wet spinning technique. The GNR was incorporated within the yarn or coating on the yarn surface by a semi-continuous layer-by-layer (LBL) technique. The light-induced shape memory effect is triggered by a low-powered laser (808 nm, 2 W for GNR-incorporated within the yarn and 1 W for GNR coated thermoplastic polyester-urethane yarn). The shape memory effect of the functionalized yarns can be triggered by laser light, and it had achieved nearly 100% strain recovery. Sabzi *et al.* [109] utilized co-electrospinning technique to simultaneously electrospin PLA

and poly(vinyl acetate) (PVAc), in the presence of GNp. The addition of GNp had contributed to the excellent triple-shape memory properties, where it increases the shape fixity and shape recovery of the PLA/PVAc. This is due to the dense physical cross-links and higher stored elastic deformation energy for the nanocomposites, in the presence of GNp.

3.4.3. Thermosetting resins

Thermosetting materials are widely used in automotive, aircraft, electronics and sports industry [110]. Thermoset-based SMPs with high heat resistance are suitable for use in high temperature environment [111]. Karger-Kocsis and Kéki [112] have documented a review of shape memory epoxies and their composites. In general, the switching or transformation temperature for thermal-activated shape memory thermosets is the T_g . The shape memory performance of epoxy can be tailored by using carbon fiber fabric [47], co-continuous phase structure of the epoxy/PCL nanoweb [113] and nanofillers. Triple-shape memory effects (TSME) for thermoset SMP can be obtained by blending, IPN and hybridization. Li *et al.* [114] prepared triple-shape memory epoxy/SiO₂ nanocomposites with bilayer structures of well-separated T_g . The epoxy/SiO₂ exhibited outstanding TSME, in which their shape fixity was improved remarkably by the addition of SiO₂ nanoparticles. Figure 10 shows the illustration of TSME of bilayer epoxy/SiO₂ nanocomposites, where ‘shape C’ is the original shape, ‘shape B’ is the first temporary shape and ‘shape A’ is the second temporary shape.

Figure 10. Illustration of triple-shape memory effect of bilayer SiO₂/epoxy nanocomposite: ‘shape C’ is the original shape, ‘shape B’ is the first temporary shape and ‘shape A’ is the second temporary shape (reproduced from Li *et al.* [114]).

According to Ortiz *et al.* [115] the photo-curable shape memory epoxy/thiol-ene/GNp nanocomposites revealed excellent values of shape recovery and shape fixity with maximum of 98 and 99%, respectively. The T_g of the co-network polyether-polythioether was function as the switching temperature. The GNp (with high thermal conductivity) and polythioethers soft domain was used to control the shape recovery and shape fixity of the epoxy nanocomposites. One of the major drawbacks of SMP is the low recovery stress, which limits the size of commercial components to a few centimeters. Consequently, the recovery stress of larger components is insufficient to counter the components’ weight. Ivens *et al.* [116] developed large-sized components based on SMP. To achieve higher recovery stresses, asymmetric fiber reinforced shape memory composites were produced using resin transfer moulding. The rate of shape recovery is higher when the fiber reinforcement is loaded in compression. This gives us an indication that the design of fiber-reinforced SMP nanocomposites should consider the fiber orientation and deformation direction.

Reversible plasticity shape memory (RPSM) property provides an alternate ‘cold’ programming approach – in which it can be programmed at temperatures well below the T_g and offers several advantages over conventional ‘hot’ programming. The RPSM can be used for large components, and often possesses a higher recovery ratio, faster recovery rate, and improved recovery stress. Abishera *et al.* [117] investigated the recovery performance of cold-programmed shape memory epoxy/CNT nanocomposites for free, partial, and completely constrained conditions. The epoxy/CNT nanocomposites achieved 100% shape recovery under free recovery conditions. Furthermore, it was found that adding CNT enhanced the shape fixity and recovery stress of the epoxy nanocomposites.

Nanofiller hybridization can be used as a feasible technique to improve the shape memory effect of polymer nanocomposites. Liang *et al.* [118] investigated synergistic effect of carbon nanofiber (CNF) and carbon nanofiber paper (CNFP) on the electro-actuation of epoxy-based SMP nanocomposites. The shape memory effect of the SMP was improved by CNFP coating due to more CNF in the conductive networks. Lu *et al.* [119] studied the combination of CNT and boron nitride on the shape memory effect

of epoxy nanocomposites. The synergistic effect of boron nitride and CNT was demonstrated to improve significantly the infrared light-induced shape recovery. It was found that boron nitrides could help to facilitate heat transfer in the epoxy nanocomposite due to improved thermally conductive property.

Thermoset blends strategy can be used to widen the application of SMP. The work from Tanpitaksit *et al.* [120] demonstrated that addition of the benzoxazine fraction could prolong the shape recovery time of the aliphatic epoxy-based SMP. The SMP achieved outstanding shape fixity value up to 99% at room temperature. At different active temperatures, *i.e.* T_g and $T_g + 20^\circ\text{C}$, the SMP needed only 1–3 minutes to fully recover to their permanent shape. The epoxy/polybenzoxazine SMP are attractive as shape-memory materials to be used in a broad range of applications such as hinge or deployable structure. This idea can be extended to SMP nanocomposites, where it is predicted that incorporation of suitable nanofiller into thermoset blends could further improve their shape-memory performance.

4. Conclusions and future perspective

In this mini-review, special attention is given on the processing and structure properties of SMP and SHP nanocomposites. The shape memory and self-healing properties of polymer nanocomposites are controlled by the selection of polymer (thermoplastic or thermoset), selection of nanofiller (pristine or surface treatment), and processing technique (*e.g.*, polymerization, melt-mixing or solution mixing). Some special preparation methods, *e.g.*, hydrogel, electrospinning, thermoset curing are suitable to develop SPN. In addition, it is worth to design SPN by readily available technology, for example, using core-shell templating [121–123], foaming [124], UV curing [125, 126], 3D and 4D printing [127, 128]. The addition of nanofiller could improve the performance of SMP and SHP nanocomposites attributed to their reinforcing-ability, nucleating-ability, and inherent functionalities (*e.g.*, thermal conductivity, electrical conductivity). The combination of smartness of the SPN, for example, SMP with SHP functionality is possible, by creating semi-IPN consisting of crosslinked thermoset, thermoplastic, and nanofiller. The key future challenges in smart polymer nanocomposites include the optimization of polymer-nanofiller interaction, dispersibility of nanofiller

in polymer matrix, and processability [129]. Multi-functional SMP and SHP nanocomposites with biocompatibility, sustainability, recyclability, ease-of-processing should be considered for future research work. Molecular simulations, phenomenological framework, micromechanical analysis, and finite element modeling can be applied to predict and optimize SPN performance [130, 131]. Innovative research on nanofillers should be able to benefit knowledge advancement in SPN. Smart polymer nanocomposites coupled with intelligent manufacturing technique will bring exciting breakthroughs and enormous development for the polymer engineering industry.

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